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XI. *The Asymmetrical Distribution of Corpuscular Radiation Produced by X-rays.*

By E. A. Owen, *B.A.* (*Cantab.*), *M.Sc.* (*Wales*), *University College, London.*

Received February 7, 1918.

According to the aether pulse theory of X-radiation, the distribution of the scattered radiation round a radiator is given by the relation $I_\theta = I_{\pi_2}(1 + \cos^2\theta)$ where I_θ is the intensity of the scattered radiation in a direction making an angle θ with the primary beam. This represents a symmetrical distribution about the plane of the radiator. Experiment shows, however, that the distribution of the scattered radiation follows this relation only on the incident side of the radiator, there being a preponderance of radiation found on the emergent side. H. A. Wilson * has shown that it is possible to account for this asymmetry on the electromagnetic pulse theory in the case of metals, by assuming that the metals are made up of minute crystals embedded in amorphous material. The scattered radiation from a metal sheet is due partly to internal reflection from these small crystals which are orientated at random, and partly to regular scattering by the amorphous portion of the metal. He shows that in this case the scattered radiation should be distributed round the radiator according to the following relation :—

$$I_\theta = A\left(\frac{1 + \cos^2\theta}{\cos\theta/2}\right) + B(1 + \cos^2\theta),$$

where A and B are constants. The first term of the expression on the right hand side of the equation arises from the regular reflection of the rays at the crystal faces, and the second term from pure scattering by the amorphous material. Wilson points out that the experimental results of Crowther † in the case of aluminium agree well with this theory if it is assumed that half the scattering is due to the crystals in the metal, and the other half to the rest of the metal supposed to be in the amorphous state, *i.e.*, when $A = B$ in the above relation.

It is well known that the same asymmetry occurs also in the case of corpuscular radiation excited when X-rays fall on a thin plate of any material. Cooksey ‡ has shown that the excess emergent corpuscular radiation for silver and gold plates is of the order of 20 per cent., and this is approximately constant when the exciting X-radiation is varied over a wide range of penetration. Philpot * later, however, found that in general an increase in hardness of the exciting radiation corresponded with an increase of asymmetry, but the increase was very slight compared with the increase in the penetrating power of the exciting radiation.

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* Wilson, Phil Mag., Vol. 27, p. 383, 1914.

† Crowther, Proc. Roy. Soc. A., Vol. 85, p. 40, 1911.

‡ Cooksey, Phil. Mag., Vol. 24, p. 37, 1912.

In view of the above explanation given by Wilson for the asymmetry observed in the case of X-rays, it is of interest to find if any difference can be detected between the ratio of emergent to incident corpuscular radiation when the screen from which the corpuscles are ejected, is changed from the crystalline to the amorphous state. A near approach to these two states can be obtained by using a screen of a salt in the dry and in the wet state respectively. The salt is held in the pores of a sheet of filter paper; in the dry state it is composed of innumerable small crystals, but when moistened it loses its crystalline nature and becomes amorphous, in which case the atoms are no longer grouped together in aggregates forming definite geometric configurations.

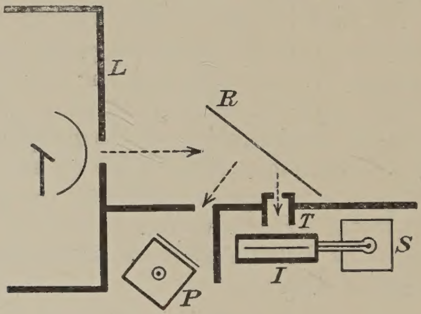

FIG. 1.

Apparatus.—The apparatus used in the investigation is sketched in Fig. 1. The rays from a platinum anticathode pass through a hole in the lead box in which the tube is enclosed, and fall on the radiator *R*. The characteristic radiation emitted by the radiator is divided into two portions, one portion passes into the primary electroscope *P*, and the other portion passes through the lead tube *T*, which cuts it down to a comparatively narrow beam. This beam enters the ionization chamber *I*, whose electrode is connected to the secondary electroscope *S*, the connecting wires being guarded by earthed tubes. The lead box and screens, and the cases of the electroscopes and the ionization chamber are also all connected to earth.

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* Philpot, Proc. Phys. Soc., Vol. 26, p. 131, 1914.

Fig. 2 shows in detail the construction of the ionisation chamber. The rays enter it through the face *P* which is a brass grid covered over with a sheet of waxed paper. The inner walls of the chamber are all covered with filter paper, so that X-rays falling on them will not give rise to an appreciable amount of corpuscular radiation. The central electrode *G* is a brass wire covered with a layer of soot, this precaution again being taken to avoid the production of corpuscular radiation, which would occur if the X-rays fell on the bare metal. The shape of the electrode is that of the chamber, rectangular in this case, and the electrode reaches within about a quarter of a centimetre of the inner walls of the

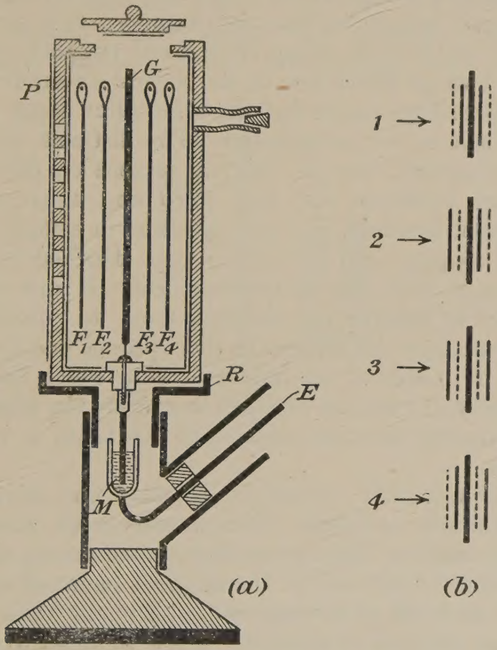

Fig. 2.

chamber. To obtain a uniform field inside the chamber, a few cotton threads rubbed with graphite were tied across the electrode.

In view of the fact that the air inside the chamber was to become laden with water vapour in the course of the experiment when the wet screens were being used, special attention was paid to the insulation of the central electrode; a plug of ambroid was used for this purpose and proved very satisfactory.

The chamber was provided with a lid by removing which the screens could be lowered into the chamber; four screens were employed which were hung from fixed supports inside the chamber, two on either side of the central electrode, of which one was pure filter paper and the other filter paper moistened with the salt to be investigated. The distance between the two inner screens, that is, the two screens on either side of the central electrode, was kept fixed and equal to 2·0 cm. The chamber was held in a fixed position in a stand, with the electrode dipping into a mercury cup attached to the wire connecting it with the electroscope leaf. It was convenient to be able to remove the chamber from its position on the stand to arrange the screens in their proper positions; after removal, by means of the bracket *R* into which the chamber fitted closely, it could be replaced in exactly the same position as it previously occupied relative to the beam of rays which entered it.

Two salts, namely, potassium bromide and silver nitrate, were examined in detail. The screens were made in the following manner. The pure filter paper screen was dipped into a saturated solution of the salt and removed after it had taken up as much of the solution as it could hold. The wet screen was allowed to stand for a few minutes to drain and its bottom edge afterwards touched with a piece of dry filter paper to remove the surplus amount of solution held by it. Readings were first taken with the screen wet. It was then dried by allowing it to stand in a current of hot air. To moisten it again when necessary, it was held in a steam bath, care being taken that too much moisture did not deposit on it. By this means the two conditions could be repeated at will and after the initial stages there was no necessity to touch the screens.

Method of Charging the Electroscopes.—As no high potential battery was available to charge the electroscopes, another method had to be employed, which would be as efficient and convenient.

Fig. 3 gives a diagram of the connections in the method finally adopted. The scheme is based on the principle of the Blake Static Machine. By this means high potentials could be obtained by using an accumulator giving only 4 volts. The accumulator drives a small sparking coil whose connections are shown in the diagram. One terminal of the secondary of the sparking coil is connected to the electrode *A*, which dips into a vertical glass tube containing a liquid of very high resistance; alcohol was used in this case but other high resistance liquids would answer the purpose equally well. Attached to the lower end of this vertical tube, is the other electrode *D*, which terminates in a point. Below this sharp point is a sphere of about half an inch radius which is connected to a variable high resistance *C*. The other terminal of this resistance is connected to the insulated charging rod of the electroscope. This second high resistance was a long piece of thread rendered conductive by lightly rubbing it with graphite, different lengths of which could be used by moving the slide *S*. The spark gap at *G* must be carefully adjusted, but once it is fixed, there is no need to readjust it, if dust is kept from depositing on the brass ball *B*. To guard against this, the tube and spark gap were enclosed in a wooden box. The electroscopes could be charged at any desired rate by adjusting the resistance *C*.

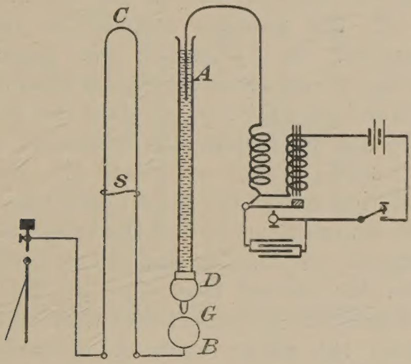

FIG. 3.

Method of Procedure.—The usual method was adopted to take readings; the deflection of the secondary electroscope was observed for a definite deflection of the primary electroscope. The characteristic radiations of the four elements, *Cu*, *Br*, *Ag* and *Sn*, were employed in the investigation; in the case of the two salts chosen the softer radiations excited only the *L* electrons of the heaviest atoms, whilst the harder radiations called out both *K* and *L* electrons. With each characteristic radiation employed, a definite cycle of operations was carried out with each salt, both in the dry and in the wet state. This cycle consisted of four steps, in each of which the screens were arranged inside the chamber in a different order. The arrangements are shown in Fig. 2 (*b*), the arrows indicating the direction of propagation of the exciting radiation.

In (1) the two salt screens are innermost, and in this case both emergent and incident corpuscular radiation enter the chamber. In (2) the incident corpuscular radiation only enters the chamber. In (3) the two filter paper screens are innermost, so that no corpuscular radiation enters the chamber. It is assumed that pure filter paper does not give rise to an appreciable amount of corpuscular radiation. In (4) only emergent corpuscular radiation enters the chamber. The incident X-radiation suffers the same absorption in each case. These observations enable us to find the values of the incident and the emergent corpuscular radiations emitted by the screens. When the screens that were at the back of the chamber were interchanged for those that were previously at the front and the above cycle of operations repeated, the ratio of emergent to incident corpuscular radiation was found to be the same as that obtained before interchanging.

The observed ratio just found does not give the true ratio required, namely that of the number of emergent corpuscles to the number of incident corpuscles emitted by a layer of the substance so thin that the exciting radiation suffers no absorption in it. In the case we are investigating there is a correction to be made for the absorption of both the X-rays and the corpuscular rays in the screens and also the absorption of the X-rays in the layer of air between the two inner screens.

Fig. 4 represents diagramatically the conditions obtaining in the experiment. Let *I* be the intensity of the X-radiation at the inner face *B* of the first salt screen whose thickness is t_1, and let μ_1 be the absorption coefficient of the rays in this screen. The rays traverse the screen in the direction of the arrows. The intensity of the rays at a depth x from the face B is given by the relation

$$I=I_x \,.\, e^{-\mu_1 x}.$$

The number of corpuscles formed in a layer of thickness dx at a depth x in the screen

$$=\kappa I_x dx=\kappa I e^{+\mu_1 x}\, dx,$$

where κ is a constant.

If β be the absorption coefficient of the corpuscles in the screen, the number of corpuscles that reach the inside of the chamber from the layer dx

$$=\kappa I e^{+\mu_1 x} dx \,.\, e^{-\beta x},$$

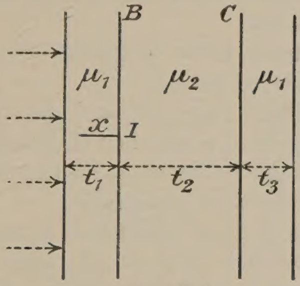

FIG. 4.

so that the total number of corpuscles entering chamber from the whole plate

$$=\kappa I \int_0^{t_1} e^{-(\beta-\mu_1)x}\, dx,$$

$$=\frac{\kappa I}{\beta-\mu_1},$$

since $e^{-\beta_1}=0$ because the screen behaves as a plate of infinite thickness to the corpuscular radiation.

Hence the observed ionisation produced by the emergent corpuscles is proportional to

$$\frac{\kappa I}{\beta-\mu_1}.$$

If t_2 be the thickness of the layer of air between the two screens, and μ_2 be the coefficient of absorption of the X-radiation in air, then the intensity of the X-radiation at C, the inner surface of the second screen, is $Ie^{-\mu_2 t_2}$. The intensity at depth x in the screen $=Ie^{-\mu_2 t_2-\mu_1 x}$. If r be the ratio of the number of corpuscles emitted in the direction in which the X-rays are travelling to that in the opposite direction from a thin layer dx, then the number of corpuscles that reach the chamber from the second screen is

$$\frac{\kappa I}{r} \cdot e^{-\mu_2 t_2 - \mu_1 x} \cdot e^{-\beta x}\, dx.$$

Total number of incident corpuscles from the whole screen

$$= \frac{\kappa I}{r} \cdot e^{-\mu_2 t_2} \int_0^{t_3} e^{-(\beta+\mu_1)x}\, dx;$$

$$= \frac{\kappa I}{r} \cdot e^{-\mu_2 t_2} \cdot \frac{1}{\beta+\mu_1}, \quad \text{since } e^{-\beta t_3} = o,$$

which is proportional to the observed ionisation produced by the incident corpuscles.

Hence r, the true ratio required, $= r_0 \cdot e^{-\mu_2 t_2} \cdot \frac{\beta - \mu_1}{\beta + \mu_1}$, where r_0 is the observed ratio.

Barkla and Collier * and Owen † have determined the absorption coefficients of a number of homogeneous X-radiations in air, so that the values of μ_2 for the different radiations here employed are directly obtainable.

There are no direct data obtainable concerning the values β and μ_1. Approximate values of these quantities may, however, be obtained from existing data. Lenard found that the absorption of fast moving cathode particles in different substances is roughly proportional to the densities of those substances. Approximate values of the absorption of the cathode rays excited by the different X-radiation used, may, therefore, be calculated from the values of the absorption coefficients in air of the corpuscular radiations produced by these characteristic X-rays. These absorption coefficients have been experimentally determined by Beatty ‡ and by Sadler.§

The values of the absorption coefficients of the X-rays in the salts employed have been calculated from the values obtained by Barkla of the absorptions of the rays in different elements, making use of the relation found by Bragg and Pierce || between the atomic number of the absorber and atomic absorption coefficient. An approximate value is obtained for the molecular absorption coefficient of the salt for each

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* Barkla and Collier, Phil Mag., Vol. XXIII., p. 987, 1912.

† Owen, Proc. Roy. Soc. A., Vol. LXXXVI., p. 426, 1912.

‡ Beatty, Phil. Mag., Vol. XX., p. 324, 1910.

§ Sadler, Phil. Mag., Vol. XXII., p. 447, 1911.

|| Bragg and Pierce, Phil. Mag., Vol. XXVIII., p. 620, 1914.

of the rays employed, from which the ordinary absorption coefficient is immediately deduced. The values employed for μ_2, β and μ_1 are given in Table I., and the correcting factors calculated for each case. The tabulated values of the correcting factors strictly apply to the dry screens, but no appreciable error is introduced by assuming them to apply also to the case of the wet screens.

The final results are collected together in Table II. The figures show that the value of the ratio of emergent to incident

TABLE I.

Exciting Radiation.	μ_2.	Potassium Bromide.			Silver Nitrate.		
		μ_1.	$\beta\times10^{-4}$.	$\frac{\beta-\mu_1}{\beta+\mu_1}\cdot e^{-\mu_2 t_2}$.	μ_1.	$\beta\times10^{-4}$.	$\frac{\beta-\mu_1}{\beta+\mu_1}\cdot e^{-\mu_2 t_2}$.
Cu	0·0109	310	11·1	0·97	607	17·4	0·97
Br	0·0039	93	5·6	0·99	212	8·8	0·99
Ag	0·0008	83	1·9	0·99	38	3·0	0·99
Sn	0·0004	14	1·4	1·00	45	2·2	1·00

TABLE II.

Exciting Radiation.	Potassium Bromide.				Silver Nitrate.			
	Wet.		Dry.		Wet.		Dry.	
	Observed ratio.	Corrected ratio.	Observed ratio.	Corrected ratio.	Observed ratio.	Corrected ratio.	Observed ratio.	Corrected ratio.
Cu	1·18	1·14	1·20	1·16	1·20	1·16	1·19	1·15
Br	1·15	1·14	1·15	1·14	1·19	1·18	1·15	1·14
Ag	1·19	1·18	1·20	1·19	1·18	1·17	1·20	1·19
Sn	1·19	1·19	1·18	1·18	1·20	1·20	1·22	1·22
Mean Values		1·16		1·17		1·18		1·17

corpuscular radiation in the case of the two salts investigated does not differ appreciably from the values obtained for this ratio by Cooksey and by Philpot in the case of gold and silver in the pure metallic state. There is an indication of an increase in the value of the ratio with increase in hardness of the exciting radiation; the variation is so slight, however, that the value obtained by taking the mean of all the values found for the ratio with the different exciting radiations, may be taken as representing a very approximate value of the ratio in each case. This mean value is practically the same for the two salts, the final mean value being 1·17, which is in good agreement with the value of the ratio found by the two above mentioned observers. Further there does not seem to be a difference in the ratio whether the salt is in the amorphous or in the crystalline state.

These results would indicate that the asymmetry observed in the case of corpuscular radiation produced by X-rays of wave-length ranging from the characteristic radiation of copper to that of tin, is practically constant and independent of the nature of the screen which emits the corpuscles, both as regards the substance of the screen and the state of that substance.

Summary.

1. The ratio of emergent to incident corpuscular radiation in the case of the two salts, potassium bromide and silver nitrate, has been investigated, when the exciting X-radiations were the characteristic radiations of copper, bromine, silver and tin.

2. The ratio has the same value whether the salt is in the wet or in the dry state.

3. The value of the ratio was found to be approximately the same for each of the two salts, and is equal to 1·17. This is approximately the same figure as that found by other observers in the case of the metals, gold and silver.

It gives me pleasure to express my appreciation of the kindly interest which Prof. A. W. Porter, F.R.S., has taken in the work.

My best thanks are due to Mr. G. G. Blake for helping me throughout the investigation.

ABSTRACT.

1. The ratio of emergent to incident corpuscular radiation in the case of the two salts, potassium bromide and silver nitrate, has been investigated, when the exciting X-radiations were the characteristic radiations of copper, bromine, silver and tin.

2. The ratio has the same value whether the salt is in the wet or in the dry state.

3. The value of the ratio was found to be approximately the same for each two of the salts, and is equal to 1·17. This is approximately the same figure as that found by other observers in the case of the metals, gold and silver.

DISCUSSION.

Dr. D. Owen said the Author's experiments bore the stamp of accuracy, and appeared to give a decisive answer to the problem proposed. On general principles, however, the observed preponderance in the number of secondary β-rays emitted on the emergent side (when X-rays fall upon a thin plate) appeared a natural result to expect. For the X-ray pulse carries not only energy, but also momentum; and the electrons within the atoms of the target or radiator experience not only transverse electric force, but also a forward impulse. On the view of a continuous wave-front, this imparted momentum may be insufficient to jerk an electron out of the atom, just as on that view the energy of the pulse has been calculated to be insufficient to produce the observed ionisation due to X-rays. On the view, however, of the existence of quanta—*i.e.*, intense condensations of activity in the wave-front—the forward momentum of the beam may be impressed like a series of hammer blows on the atoms of the target. A simple calculation shows that appreciable effects in this respect may well occur—*e.g.*, in the case of radiation of the intensity of full sunlight the momentum communicated would, if wholly spent in ejecting electrons on the emergent side, be sufficient to generate 10^{15} electrons per square centimetre per second, each with a velocity of 10^9 cm. per second.

Dr. H. S. Allen said that if he understood the Paper rightly, the result that Mr. Owen has found—viz., that the ratio of emergent to incident corpuscular radiation is the same in the amorphous as in the crystalline state, renders doubtful the explanation of asymmetry put forward by H. A. Wilson. In his opinion an explanation of a more fundamental character was required than that which attributes the asymmetry of the scattered radiation to the difference between the behaviour of crystalline and amorphous material. In this connection a recent Paper by A. H. Compton ("Journ." Wash. Acad. Sci., January 4, 1918) is of considerable interest. He assumes that the electron is in the form of a spherical shell, each part of which can scatter independently, and may be capable of rotational motion. He shows that it is then possible to explain not only the asymmetry of the scattered rays, but also the diminution of scattering with decrease of wave length. Since the mass of an electron cannot be accounted for on the basis of a uniform distribution of electricity over the surface of a sphere, Mr. Compton suggests that the true shape of the electron may be that of a ring, having an effective radius many times greater than that ordinarily accepted. Mr. Compton's estimate of the radius is $2{\cdot}3 \times 10^{-10}$ cm., but if some recent measurements by Sir Ernest Rutherford are used in the calculation, this estimate must be reduced to about one-tenth of the value stated ("Nature," Vol. C., p. 510, 1918). If this hypothesis of a ring electron be accepted, the electron may act as a small magnet, as suggested by A. L. Parson, and this explains Forman's effect of magnetisation of iron upon its absorption coefficient.

Mr. T. Smith thought the initial equation with which the Paper started was somewhat extraordinary. It was difficult to see what physical considerations gave rise to the factor $\cos \frac{1}{2}\theta$ in the denominator of an equation which he presumed was intended to apply from 0 deg. to 180 deg.

The Author, in reply, said that if the asymmetry is to be attributed to the pressure of radiation, one would expect that the value of the ratio obtained for the asymmetry would vary with the intensity of the exciting X-radiation. It has been shown, however, by Philpot that this is not the case, the value of the ratio remaining the same for radiations of the same wave-length whether a beam of X-rays direct from a bulb or a beam of characteristic rays from a metal plate, were employed to excite the corpuscular radiation; the intensity of the radiation would be much greater in the former than in the latter case. The results of the present Paper show that the explanation put forward by Wilson to explain the asymmetry in the case of X-radiation does not appear to be adequate to explain the asymmetry in the case of corpuscular radiation. He agreed with Dr. Allen that an explanation of a more fundamental character is necessary to account for this phenomenon.

XII. *On " Air Standard " Internal Combustion Engine Cycles and their Efficiencies.* *By* Charles H. Lees, *D.Sc., F.R.S.*

Received February 18, 1918.

1. In accordance with the recommendations of the Committee of the Institution of Civil Engineers on the Standards of Efficiency of Internal Combustion Engines* it has become the practice to compare the thermal efficiency of any internal combustion engine with that of an ideal standard engine taking in and giving out its heat in as nearly as possible the same way as the actual engine, using as working substance a perfect gas, and subject to no losses due to friction or to conduction or radiation of heat from the working substance. Such an ideal engine using air, which for the purpose in view may be taken as a perfect gas, the Committee calls an " Air Standard " engine.

In such an ideal engine the heat produced by the explosion of the charge is supposed to be communicated to the working substance without changing the physical properties of that substance, the expansion which follows is taken as strictly adiabatic, the exhaustion and re-charge of the cylinder are supposed to occur instantaneously at the end of the working stroke, or the working substance is supposed to remain the same but to have sufficient heat taken from it to reduce its temperature and pressure to those existing at the beginning of the compression stroke, which in turn is supposed to be strictly adiabatic.

2. Two of the processes which take place during the cycle of operations are thus seen to be adiabatic, while the other two processes by which the working substance is brought from one adiabatic to the other may be of any type, either the same or different, so long as they are not adiabatic. Up to the present time the only other processes which have been considered in the discussions of the thermal efficiencies of Air Standard internal combustion engines are those at :—

(*a*) constant temperature ;
(*b*) constant pressure ;
(*c*) constant volume.

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* Proc. Inst. Civil Eng., Vol. CLXII., p. 507 (1905) and Vol. CLXIII., p. 241 (1906). The Committee consisted of Profs. Ashcroft, Callendar and Dalby, Sir Dugald Clerk, Mr. Hayward, Sir Alexander Kennedy, Capt. Sankey and Mr. Wilson.

The first give with the two adiabatic strokes the Carnot cycle, the second give a cycle partially followed in the Diesel engine, while the third give the Otto and the Clerk cycles.

It is pointed out in the Report of the Committee on the Standards of Efficiency that for each of these cycles the expression for the efficiency is the same,* viz. :—

$$\text{efficiency}=1-(1/r)^{\gamma-1},$$

where γ is the ratio of the specific heats of the working substance at constant pressure and at constant volume respectively and r is the ratio of the volume of the substance before to that after the compression stroke a ratio, known as the "compression ratio."

3. It is one of the objects of the present Paper to show that the efficiencies of a much more extensive class of cases than the three named in the Committee's Report are expressed by the same function of the "compression ratio."

We shall assume that the adiabatic curve of the working substance is given by

$$pv^{\gamma}=\text{constant},$$

where p is the pressure and v the volume, and that the constant has the value C at the expansion and c at the compression stroke. We shall take the curves for the periods of absorption and rejection of heat which complete the cycle to be of the form

$$pv^{a}=\text{constant},$$

where a is a constant not identical with γ and the constant on the right of the equation has the value A for the explosion and a for the exhaust curve. Writing the values of the pressure and volume at the end of the compression $p_0 v_0$, at the end of the heat absorption $p_1 v_1$, at the end of the adiabatic power stroke $p_2 v_2$, and after heat rejection $p_3 v_3$, we have (Fig. 1) :—

$$p_0v_0^{a}=p_1v_1^{a},\quad p_1v_1^{\gamma}=p_2v_2^{\gamma},\quad p_2v_2^{a}=p_3v_3^{a},\quad p_3v_3^{\gamma}=p_0v_0^{\gamma}.$$

Multiplying together these equations we get

$$p_0p_1p_2p_3v_0^{a}v_1^{\gamma}v_2^{a}v_3^{\gamma}=p_1p_2p_3p_0v_1^{a}v_2^{\gamma}v_3^{a}v_0^{\gamma},$$

or $\qquad v_1v_3=v_0v_2,\quad$ that is, $\quad v_3/v_0=v_2/v_1,$

or the compression ratio along the compression adiabatic is equal to the expansion ratio along the expansion adiabatic.

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* Proc. Inst. Civil Eng., Vol. CLXII., p. 325 (1905). The author of this simple expression for the efficiencies in the three cases is not indicated in the report, but according to Sir Dugald Clerk, "The Gas, Petrol and Oil Engine," new edit., Vol. I., note p. 83, it was first pointed out to the Committee by Prof. Callendar.

Writing the equation $v_1/v_0=v_2/v_3$ it is seen that equality of ratio holds also along the two α curves.*

4. The efficiency of the cycle is equal to $1-H_{23}/H_{01}$ where H_{23} is the heat given up by the working substance in the path from p_2v_2 to p_3v_3, and H_{01} the heat taken in by it in the path from p_0v_0 to p_1v_1. In each case the heat is measured in work units by the area enclosed by the path, and those parts of the two adiabatics through the ends of the path which lie to the right of the path.

The area included between the ordinate of the point p_3v_3, the axis of volume and that part of the adiabatic $pv^{\gamma}=c$ through the point which lies to the right of it, is $\dfrac{p_3v_3}{\gamma-1}$.

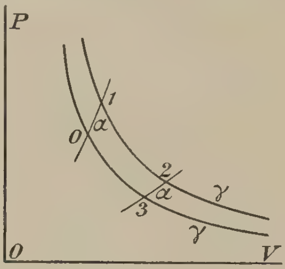

FIG. 1.

Curve 1–2 adiabatic $pv^{\gamma}=C$. 0–1 $pv^{\alpha}=A$.
" 0–3 " $pv^{\gamma}=c'$. 3–2 $pv^{\alpha}=a$.

That between the ordinate of the point p_3v_3, the curve $pv^{\alpha}=a$ between p_3v_3 and p_2v_2 and the ordinate of the latter point is $\dfrac{(p_2v_2-p_3v_3)}{\alpha-1}$, which reduces to $p_3v_3\log(v_2/v_3)$, if $\alpha=1$.

In the general case the area between the curve $pv^{\alpha}=a$ through the points p_3v_3, p_2v_2, and those portions of the adiabatics through the same points lying to the right of them is therefore

$$=(p_2v_2-p_3v_3)\left(\frac{1}{\alpha-1}-\frac{1}{\gamma-1}\right).$$

Hence this expression is the H_{23} of the efficiency formula. It reduces to $p_3v_3\log(v_2/v_3)$ if $\alpha=1$.

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* These relations, as well as the corresponding ones connecting the pressures, are readily seen from a diagram with $\log v$ and $\log p$ as co-ordinates.

In the same way it is seen that

$$H_{01}=(p_1v_1-p_0v_0)\left(\frac{1}{\alpha-1}-\frac{1}{\gamma-1}\right),$$

which reduces to $p_0v_0\log(v_1/v_0)$ if $\alpha=1$.
Hence the efficiency of the cycle becomes

$$1-\frac{(p_2v_2-p_3v_3)}{(p_1v_1-p_0v_0)}.$$

That is since $p_2v_2{}^\alpha=p_3v_3{}^\alpha$, $p_1v_1{}^\alpha=p_0v_0{}^\alpha$, and $v_2/v_3=v_1/v_0$

$$1-p_3v_3/p_0v_0.$$

Or finally since $p_3v_3{}^\gamma=p_0v_0{}^\gamma$, the efficiency may be written

$$1-(v_0/v_3)^{\gamma-1}\quad\text{or}\quad 1-\left(\frac{1}{r}\right)^{\gamma-1}\quad\text{where}\quad r=\frac{v_3}{v_0}.$$

The special value $\alpha=1$ leads to the same expression.

Thus a cycle composed of two adiabatics and two curves of the form $pv^\alpha=$constant, where α is a constant which may have any value, positive or negative, so long as it is the same for the two curves, has an efficiency$=1-(1/r)^{\gamma-1}$, where r is the compression ratio measured along either adiabatic.

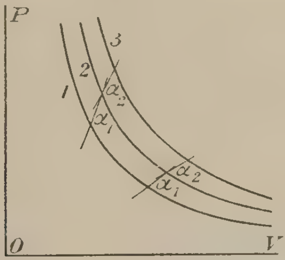

Fig. 2.

Curves 1, 2, 3 adiabatics $pv^\gamma=$constant.
α_1, α_2, values of α for curves $pv^\alpha=$constant.

This general law includes the three cases for which the expression was previously known to hold, *i.e.*, for constant temperature ($\alpha=-1$), constant pressure ($\alpha=0$), and constant volume ($\alpha=\infty$).

5. If a third adiabatic is drawn and we designate the three in order of distance from the origin the first, second and third adiabatic respectively (Fig. 2) we may take two points on the first adiabatic for which the compression ratio r has a given value, and can draw through each of these points a curve of

the class $pv^{\alpha}=\text{constant}$ with the special value α_1 for α. These curves will cut the second adiabatic in points which have the same compression ratio, r, as the first pair of points. Through each of the points on the second adiabatic we can draw a second curve $pv^{\alpha}=\text{constant}$, with $\alpha=\alpha_2$. These will cut the third adiabatic in points for which the compression ratio still has the same value r. The process may be continued to, say, the nth adiabatic. Between the first and the nth adiabatic we now have a cycle whose explosion and exhaust curves are made up of portions of curves of the type $pv^{\alpha}=\text{constant}$ with the values of α for the successive portions of curve chosen in any way we desire. The efficiency of the cycle is still given by $1-(1/r)^{(\gamma-1)}$ where r is the compression ratio along any of the adiabatics. The number of intermediate adiabatics and the value of α between each pair may be so chosen that any prescribed curve for either the explosion or for the exhaust may be followed as closely as we desire.

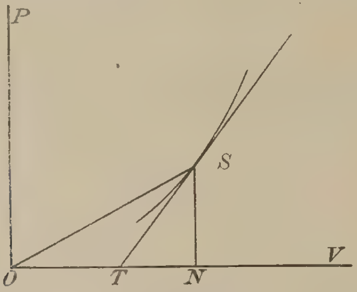

Fig. 3.—Determination of α for Curve and Cotstruction of Curve with given α.

If, for instance, $p=f(v)$ is the curve with which $pv^{\alpha}=\text{constant}$ is to be made to coincide in the neighbourhood of the point p_0v_0, we make $pv^{\alpha}=p_0v_0^{\alpha}$ to secure that the α curve passes through the point p_0v_0 and the slope upwards $-\alpha p_0/v_0=f'(v_0)=\tan\theta_0'$, where θ_0' is the angle which the tangent to the given curve at the point p_0v_0 makes with the axis of volumes. This gives $\alpha=-\tan\theta_0'/\tan\theta_0$, where θ_0 is the angle which the radius vector to the point p_0v_0 makes with the axis of volumes (Fig. 3) or if N is the foot of the perpendicular from the point S on to the axis of volumes and T is the point in which the tangent to the curve at S cuts that axis, $\alpha=-ON/TN=ON/NT$, where the subtangent NT is regarded as positive if T lies on the further side of N from O.

If a is given the curve $pv^a =$ constant through a given point may be drawn in steps by the same construction.

If the curve which has not been used in selecting the values of a be now drawn with the values of a thus determined we have a cycle which still has the efficiency $1-\left(\frac{1}{r}\right)^{(\gamma-1)}$.

Thus an "air standard" cycle composed of two adiabatics $pv^\gamma=$constant, and either an explosion curve or an exhaust curve of any prescribed form, the curve not prescribed being drawn with the values of a determined for the prescribed curve, will have its efficiency given by $1-(1/r)^{\gamma-1}$, where r is the compression ratio measured along either adiabatic.

6. In applying this theorem to any "air standard" cycle composed of two adiabatics and two other curves crossing them which may for convenience be called the explosion and exhaust curves respectively, it is best to select values of a which will reproduce as closely as it is desired the explosion curve $ABCD$ (Fig. 4), and with these values of a to draw the exhaust curve $A'B'C'D'$ to correspond. If this is done the efficiency of the actual cycle can be readily determined. For the efficiency of the cycle $ABCDD'C'B'A'$ with corresponding explosion and exhaust curves is given by $1-(1/r)^{\gamma-1}$, where r is the ratio of compression measured along either adiabatic, and γ is the exponent for the adiabatic. This expression is the ratio of the area enclosed by the cycle $ABCDD'C'B'A'$

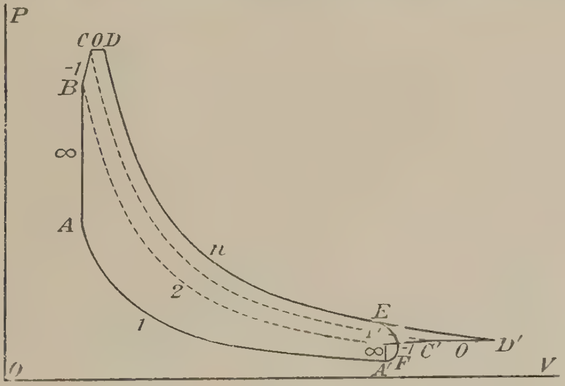

FIG. 4.

Curves 1, 2, ... n adiabatics $pv^a =$ constants. $ABDEF$ actual cycle. $ABDD'C'A'$ cycle with corresponding explosion and exhaust curves. ∞, -1 and O are the values of a for the lines against which they are written.

to the area which represents in work units the heat taken in by the working substance along the explosion curve *ABCD*. In the same manner the efficiency of the actual cycle *ABCDEFA′* is the ratio of the area enclosed by that cycle to the heat taken in along the explosion curve. Hence as the two explosion curves have been made identical, as nearly as desired, the efficiency of the actual cycle is

$$\left\{1-\left(\frac{1}{r}\right)^{\overline{\gamma-1}}\right\}\frac{\text{area of actual cycle } ADEF}{\text{area of cycle } ADD'B' \text{ with exhaust curve with same } a \text{ values as explosion curve.}}$$

For many purposes a sufficiently close approximation to the actual explosion curve may be secured by taking in succession a constant volume line, a line through the zero of volume and pressure, and a constant pressure line as at *ABCD* (Fig. 4). These lines are easily drawn and can be so selected that the area enclosed by them and the actual curve is as much on one side of them as on the other.

ABSTRACT.

It is well known that the efficiency of an air standard internal combustion engine working through a cycle bounded by two adiabatics, and either two isothermals, two constant volume lines or two constant pressure lines is given by $1-(1/r)^{\gamma-1}$ where r is the compression ratio and γ is the ratio of the two specific heats of air.

In the present Paper it is shown that the efficiency is given by the same expression if the cycle is composed of two adiabatics and two curves $pv^a=A$, $pv^a=a$, where a has any positive or negative value and A and a are constants. Since a may be chosen so that any explosion curve may be followed as closely as desired by short lengths of a curves, a cycle can be drawn with the above efficiency and any prescribed explosion curve. The ratio of the efficiency of a cycle with prescribed explosion and exhaust curves to that of the cycle so drawn is shown to be the ratio of the two areas on the indicator diagram. The thermal efficiency of a cycle with prescribed explosion and exhaust curves is therefore readily found.

DISCUSSION.

Dr. D. OWEN asked what the ratio of the efficiencies of the actual and theoretical cycles was in practice.

Dr. H. S. ALLEN asked if it was not possible to generalise the result established in the Paper, and to say that the expression for the efficiency held when the explosion curve is represented by $f(p, v)=\text{constant}$, where $f(p, v)$ is any function of p and v, provided the equation for the exhaust curve is suitably chosen.

Prof. LEES, in reply, said the ratio of the actual cycle to the other was usually 0·9 to 0·95. Dr. Allen's suggestion was quite correct. He had aimed, however, at expressing the result in a form suitable for graphical calculation.

XIII. *Cohesion* (*Fourth Paper*). *By* HERBERT CHATLEY, *D.Sc.* (*Lond.*).

RECEIVED FEBRUARY 25, 1918.

THE aim of the present Paper is to consider the value of molecular force as indicated by Van der Waals' gas formula (particularly at the critical state where the liquid and gaseous states merge), and to relate the results to the previous inquiry.

The results of the investigation may be summarised as follows :—

1. Van der Waals' formula implies that molecular attraction varies inversely as the fourth power of the molecular interval.* Incidentally it may be mentioned that it also indicates the repulsion as varying inversely as the molecular interval, except for very small intervals, where it varies as the square of the interval divided by the difference between the cubes of the interval and of the interval at absolute zero, but also depends on the thermal energy involved.

2. The approximate accuracy of Van der Waals' formula at the critical state provides a further disproof of Kelvin's Newtonian theory of molecular attraction.

3. The author's formula,†

$$t_2 = Gm^2/d^{2+4\frac{d_0}{d}},$$

is apparently not irreconcilable with the actual values of the molecular attraction at the critical state.

4. Certain modifications must be introduced in the Van der Waals' formula to make it agree exactly with the facts.

1. *Deductions from Van der Waals' Formula.*

It is well known that this formula is arrived at as follows :—

$$\left\{\begin{matrix}\text{Ideal unrestricted}\\ \text{kinetic gas pressure}\end{matrix}\right\}\left\{\begin{matrix}\text{Clear volume in}\\ \text{one mol of gas}\end{matrix}\right\}=RT,$$

or

$$\left\{\begin{matrix}\text{Actual gas pressure + pressure}\\ \text{due to molecular centripetal}\\ \text{attraction of the whole mass}\end{matrix}\right\}\left\{\begin{matrix}\text{Actual molar}\\ \text{volume}-\text{net volume}\\ \text{of molecules}\end{matrix}\right\}=RT,$$

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* The term interval here means the distance from centre to centre.

† *Vide* "Cohesion," third Paper.

which was written by Van der Waals as

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT.$$

This is a cubic equation in terms of v, and at the critical state the three roots are equal, and we have the following relations

$$a=27b^2p_c=3p_cv_c^{\,2}=\frac{27RT_cb}{8}=\frac{9}{8}RT_cv_c=\frac{27R^2T_c^{\,2}}{64p_c},$$

$$b=\frac{v_c}{3}=\frac{RT_c}{8p_c},$$

and also

$$p_cv_c=\tfrac{3}{8}\,.\,RT_c,\text{*}$$

and

$$\frac{a}{v_c^{\,2}}=3p_c\,;\;\; p_c'=p_c+\frac{a}{v_c^{\,2}}=\frac{RT_c}{v_c-b}=4p_c,\text{ so that }\frac{p_c'}{p_c}=4\text{ and }\frac{p_c'}{\dfrac{a}{v_c^{\,2}}}=\frac{4}{3}.$$

Assuming no expansion of the actual molecules, $b=v_0$, the molar volume at absolute zero, and so we find that at the critical state the molecular interval

$$d_c=\sqrt[3]{3}\,.\,d_0=1{\cdot}442d_0,$$

and, assuming cubic spacing, $d_0=\sqrt[3]{\frac{b}{N}}$, where N is Avogadro's number (molecules per gram-molecule).

The radius of the molar sphere whose volume is v, is

$$r=\sqrt[3]{\frac{3v}{4\pi}},$$

and the density $D=M/v$.

The number of molecules per square centimetre

$$=\left(\frac{N}{v}\right)^{\frac{2}{3}}=\frac{1}{d^2}=n^2.$$

The attraction on a single molecule at the surface of the molar sphere due to all the N molecules in it, is then, according to Van der Waals,

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* This formula, assuming Van der Waals' equation is true, expresses the relation for the production of critical volume at high temperatures and pressure. Thus, for hydrogen, $T_c=2{\cdot}354\times10^{-6}p_c$, where p_c is in dynes per square centimetre. If p_c is 10^{10}, $T_c=23{,}540°$ *abs.*, or, say, 23,250°C. The Bridgman solar and planetary liquids doubtless occur under some such pressures and temperatures.

$$t=\frac{\frac{a}{v^2}}{n^2}=aN^{-\frac{2}{3}}v^{-\frac{4}{3}};$$

and, since the molecular interval $d=\sqrt[3]{\frac{v}{N}}$,

$$t=aN^{-2}d^{-4}.$$

Van der Waals' equation, therefore, implies that the attraction of the whole gram molecule (on one molecule) varies inversely as the fourth power of the molecular interval.

For CO_2, the value of a as computed from p_c and T_c is $3{\cdot}6\times 10^{12}$, so that if d is 10^{-7},

$$t=\frac{3{\cdot}6\times 10^{12}}{36\times 10^{46}\times 10^{-28}}=10^{-7} \text{ dynes.}$$

It must be observed that this is the attraction due to N molecules acting on one superficial molecule, and not that between one pair of molecules. All except a few, however, are very remote from the one considered, and therefore contribute only slightly to the total force. The effective distance of the whole mass when the law of attraction is *not* the inverse square is *not* the radius of the sphere.

2. *Comparison with the Newtonian Law.*

If the Newtonian law were applicable, as Kelvin thought, then we should have (M=molecular weight)

$$t_1=\frac{GMn^2m}{r^2}=\frac{GM^2}{N^{\frac{1}{3}}\left(\frac{3v}{4\pi}\right)^{\frac{2}{3}}} \text{ per square centimetre.}$$

This disagrees dimensionally with Van der Waals' form. Using the actual critical value of v for CO_2

$$t_1=1{\cdot}844\times 10^{-13} \text{ dynes per square centimetre,}$$

or, $2{\cdot}624\times 10^{-29}$ dynes per superficial molecule, whereas the actual molecular attraction as computed from the critical values of volume, pressure and temperature is $3{\cdot}784\times 10^{8}$ dynes per square centimetre, or $8{\cdot}744\times 10^{-7}$ dynes per molecule, making the ratio

$$\frac{\text{molecular attraction}}{\text{Newtonian attraction}}=3{\cdot}33\times 10^{22}.$$

This may be compared with the ratio of 10^{30}, which is given in "Cohesion" (second Paper) for the solid state. Kelvin's hypothesis thus appears to be decisively controverted. Further values of the attractions are given in the attached table.

The apparent discrepancy of considering here the attraction of many molecules upon one, whereas in the analysis of the solid state only single pairs were taken is partially explained by the fact that in the gas or even in the liquid there are repeated collisions, successively bringing many molecules into close proximity with the one in question.

3. *Comparison with the Author's Formula.*

It seems impossible to integrate the attraction of a sphere when the index of the molecular interval varies, but quantitatively the values given by the author's formula for small distances appear to be not impossible. The approximate accuracy of Van der Waals' formula for large values of v, in spite of the fact that the author's formula then indicates the Newtonian condition, is possibly also explicable by the state of repeated collision, although at or near the critical condition the collisions will mostly occur between the same pairs.*

At the critical state a comparison of the actual molecular attraction with that obtained by the author's formula shows that the attraction of the N molecules (whose centre is at a distance r from the superficial molecule) is from 10^8 to 10^{21} times that of a single molecule at the molecular interval. Since N is $6{\cdot}06 \times 10^{23}$, this shows a fair agreement, but the question needs to be further investigated.

The following formula is used to compute the actual attractions :—

$$p_c(1+A) \,.\, v_c(1-B)=RT_c,$$

and experimentally $p_c v_c = kRT_c$,

$$A=\frac{1}{(1-B)k}-1\,;$$

the attraction per superficial molecule $=Ap_c d_c^2$.

At absolute zero there is very good agreement.

4. *Corrections to Van der Waals' Formula.*

The discrepancies of the Van der Waals' formula at the critical state are as follows :—

(*a*) The irreducible volume is too large.
(*b*) The critical volume is too large.
(*c*) The ratio $p_c v\ /RT_c$ is too large.

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* See footnote on next page.

The quantities a and b must, therefore, be reduced slightly, but the differences vary with different substances.

The index of v in the attraction term is certainly incorrect for very large values of v, although as mentioned above, the continuous series of temporary close contacts in collision may mask this error.*

The table which follows shows the principal results which can be obtained along these lines. It is hoped to proceed further and connect the conditions with those in the solid state. However this may be, it seems clear that Van der Waals' hypothesis throws important light on the question of molecular astronomy.

TABLE OE DATA.

Substance.	H_2.	H_2O.	CO_2.	SO_2.	$SnCl_4$.
olecular weight	2·0155	18·0155	44·00	64·10	260·3
itical pressure ; Atmospheres.	13·4	217·5	72·9	77·70	36·95
itical temp. : Absolute	31·0	647·0	304·1	430·3	591·8
itical volume : v_c cubic cm.	60·45	45·00	98·22	125·00	351·00
tto from V. der W.s' equat.	72·10	91·50	128·30	170·30	492·60
rom p_c and T_c	$0{\cdot}21\times10^{12}$	$5{\cdot}537\times10^{12}$	$3{\cdot}651\times10^{12}$	$6{\cdot}853\times10^{12}$	$13{\cdot}436\times10^{12}$
rom p_c and T_c	24·03	30·49	42·77	56·7	164·2
=one-third critical volume	20·15	15·00	32·74	41·67	117·0
=volume at abs. zero	22·4	18·02	$<29{\cdot}33$	$<44{\cdot}83$	$<114{\cdot}1$
itical density, D_c	0·033	0·4	0·448	0·513	0·7419
nsity at abs. zero, D_0	0·09	1·0	1·5	$>1{\cdot}43$	$>2{\cdot}28$
$/D_0=v_0/v_c=B$	0·36	0·4	0·299	$<0{\cdot}263$	$<0{\cdot}232$
$_c/RT_c=K$	0·3217	0·1845	0·2869	0·2749	0·2670
from K and B	3·856	8·036	3·980	3·935	3·876
$\div p'_c$	0·2059	0·1107	0·2008	0·2027	0·2051
$\div Ap_c$	1·26	1·125	1·251	1·254	1·258
$\overline{1/B}=d_c/d_0$	1·397	1·257	1·489	1·561	1·628
$=\sqrt[3]{v_c/N}$	$3{\cdot}331\times10^{-8}$	$4{\cdot}203\times10^{-8}$	$5{\cdot}451\times10^{-8}$	$5{\cdot}907\times10^{-8}$	$8{\cdot}835\times10^{-8}$
	$1{\cdot}673\times10^{-8}$	$3{\cdot}344\times10^{-8}$	$3{\cdot}660\times10^{-8}$	$3{\cdot}784\times10^{-}$	$5{\cdot}121\times10^{-8}$
$=M/N$, gr.	$3{\cdot}326\times10^{-24}$	$2{\cdot}973\times10^{-23}$	$7{\cdot}259\times10^{-23}$	$1{\cdot}058\times10^{-22}$	$4{\cdot}294\times10^{-22}$
^{2} dynes	$7{\cdot}30\times10^{-55}$	$5{\cdot}833\times10^{-53}$	$3{\cdot}557\times10^{-52}$	$7{\cdot}387\times10^{-52}$	$1{\cdot}53\times10^{-50}$
m^2 dynes	$4{\cdot}415\times10^{-31}$	$3{\cdot}536\times10^{-29}$	$2{\cdot}156\times10^{-28}$	$4{\cdot}417\times10^{-28}$	$9{\cdot}27\times10^{-27}$
$=\sqrt[3]{3v_c/4\pi}$ cm.	2·453	2·207	2·866	3·101	4·376
$=GNm^2/r^2$ dynes	$7{\cdot}336\times10^{-32}$	$7{\cdot}259\times10^{-30}$	$2{\cdot}624\times10^{-29}$	$4{\cdot}593\times10^{-29}$	$4{\cdot}841\times10^{-28}$
$=Ap_c/n_c^2=Ap_cd_c^2$ dynes	$1{\cdot}127\times10^{-8}$	$3{\cdot}130\times10^{-6}$	$8{\cdot}744\times10^{-7}$	$1{\cdot}079\times10^{-6}$	$1{\cdot}009\times10^{-6}$
$\div F_2$	$1{\cdot}535\times10^{24}$	$4{\cdot}311\times10^{23}$	$3{\cdot}332\times10^{22}$	$2{\cdot}35\times10^{22}$	$2{\cdot}084\times10^{21}$
$2+(4d_0/d_c)$	4·869	5·183	4·692	4·563	4·458
$=Gm^2/d_c\gamma$ dynes	$1{\cdot}299\times10^{-29}$	$9{\cdot}961\times10^{-15}$	$4{\cdot}280\times10^{-18}$	$7{\cdot}122\times10^{-19}$	$5{\cdot}538\times10^{-19}$
$=F_1/F_3$	$8{\cdot}672\times10^{21}$	$3{\cdot}142\times10^{8}$	$2{\cdot}043\times10^{11}$	$1{\cdot}516\times10^{12}$	$1{\cdot}822\times10^{12}$
N	$1{\cdot}430\times10^{-2}$	$5{\cdot}183\times10^{-16}$	$3{\cdot}370\times10^{-13}$	$2{\cdot}500\times10^{-12}$	$3{\cdot}004\times10^{-12}$
$=a/N^2d_0^4$ dynes	$4{\cdot}645\times10^{-7}$	$1{\cdot}206\times10^{-5}$	$5{\cdot}537\times10^{-6}$	$9{\cdot}093\times10^{-6}$	$5{\cdot}315\times10^{-6}$
$=Gm^2/d_0^6$ dynes	$5{\cdot}35\times10^{-10}$	$4{\cdot}176\times10^{-8}$	$1{\cdot}122\times10^{-7}$	$2{\cdot}517\times10^{-7}$	$8{\cdot}285\times10^{-7}$
$=F_4/F_5$	868	288·8	49·33	10·01	6·415

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* A further discrepancy, which is here very serious, is that the attraction on the inner molecules effectively reduces their kinetic pressure on the outer ones, and so has the effect of apparently increasing the attraction on the outer ones.

ABSTRACT.

The Paper is the fourth of a series dealing with the subject of Cohesion. The aim of the present Paper is to consider the value of molecular force as indicated by Van der Waals gas formula (particularly at the critical state where the liquid and gaseous states merge), and to relate the results to the previous enquiry.

DISCUSSION.

Dr. H. S. ALLEN (communicated): In this Paper Prof. Chatley has pointed out a number of interesting relations depending on the equation of Van der Waals. It is more than doubtful whether any attempt to found a theory on purely central attractions and repulsions varying as some power of the distance can prove adequate to explain the facts. It is certain that the law of attraction at molecular distances is not that of the inverse square of the distance. In a lengthy series of Papers in the "Philosophical Magazine," Sutherland,* whose work has not received adequate recognition, has discussed the law of the inverse fourth power, and has pointed out the relation which it bears to the characteristic equations of Van der Waals and others. A useful summary of work on the subject is given by W. C. McC. Lewis, in his "System of Physical Chemistry" (Longmans, 1916). It may be mentioned that Lewis† has examined the connection between the internal pressure or cohesion, π, in the equation

$$(p+\ )(v-b)=RT,$$

and the dielectric capacity and permeability of a liquid. He has shown that the Obach Walden relation regarding the proportionality between the internal pressure and the dielectric constant follows from the hypothesis that molecular attraction is electromagnetic, not electrostatic in nature. That cohesion arises from the action of electric or electro-magnetic forces may be inferred from optical experiments. The Lorentz-Fitzgerald hypothesis explains the negative result of the Michelson-Morley experiment by a contraction of the material framework of the apparatus in the direction of its motion through the aether. Such a contraction may be predicted from the standpoint of electromagnetic theory. There is, therefore, a strong presumption that "the forces of cohesion between the particles, which give a solid its rigidity, are electrical forces."‡

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* Sutherland, "Phil. Mag.," Vol. 24, p. 113, p. 168, 1887; Vol. 35, p. 211, 1893.

† Lewis, "Phil. Mag.," Vol. 28, p. 104, 1914.

‡ Eddington, "Nature," Vol. 101, p 15, 1918.

XIV. *Notes on the Pulfrich Refractometer.* *By* J. Guild, *A.R.C.Sc., D.I.C., F.R.A.S. (from the National Physical Laboratory).*

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§ 1. Introduction.

Almost all the commercial testing of optical glass is carried out on the instrument known as the Pulfrich Refractometer, the general principles of which are sufficiently well known to render a description of the usual type of instrument superfluous. Considerable experience in the use of this refractometer has led the author to form a very high opinion of its potentialities, but a very much poorer one of the performance of the actual instrument as turned out by Messrs. Zeiss—until recently the only makers. This is in large part due to the fact that work of the accuracy now attempted with the instrument was probably not contemplated by the designer, who most likely had in view the requirements of the chemist rather than those of the optician. The increasing demands of the computer of optical systems for high accuracy in the refractometry of the glasses he has to employ makes it essential that an accurate and at the same time rapid method for the refractometry of glass should be available. The Pulfrich method is the only one as far as the author is aware in which the desired accuracy is approached without the expenditure of an excessively large amount of time on each test. The purpose of these notes is to point out some of the reasons for the defective performance of existing refractometers and to suggest modifications in the design and precautions in the use of the instrument which will help considerably towards the attainment of the theoretical accuracy.

§ 2. Potentialities of Pulfrich Refractometer.

As users of the instrument are aware, settings are made by means of a micrometer tangent screw of which the drum is subdivided to tenths of a minute. Experience shows that when the substance under test is satisfactory as regards homogeneity and surface, settings can be repeated without difficulty to a tenth of a minute. This corresponds approximately to an accuracy of 0·00001 in the refractive index of the specimen; consequently the instrument ought, if free from all sources of error other than the uncertainty of setting, to give results accurate to one unit in the fifth decimal place.

In practice one finds that instead of realising this accuracy results are frequently in doubt in the fourth place, while the dispersions, *i.e.*, the differences between the indices for different wave-lengths, although measured on the run of the micrometer, are not obtainable with a *certainty* of better than three units or thereabouts in the fifth place. This, of course, is apart from any systematic errors due to erroneous constants for the block of the instrument, calibration errors in the scales, faulty disposition of the various parts, &c. In the presence of such errors much more serious discrepancies may arise.

§ 3. Non-Systematic Errors.

Instrumental Defects.—One of the worst features of the Zeiss Pulfrich refractometer is the coarse and irregular dividing of the scale of the circle. This makes it impossible to obtain satisfactory observations when co-ordinating the circle readings with those of the micrometer, and contributes largely to the uncertainty in the final result for the absolute index. This can only be reduced to within reasonable limits by tedious repetition of circle readings—more than there is time for in routine test work. The dividing of the circle and vernier should be of the finest possible quality, and the diameter of the circle could profitably be increased to 6 inches or even more.

The micrometer screw and fittings are of poor design. The split nut in which the screw works is much too short, with the result that it is impossible to adjust the tightness so as to have the screw moving without shake, but at the same time freely, over its whole range. Moreover, on account of the leverage of the screw, it soon works loose after being tightened up ; so one is either working with a rather tight screw or a shaky one—both of which conditions are inimical to accuracy ; although, with proper caution to avoid backlash, the shaky condition is the lesser evil. These are the chief sources of non-systematic error due to instrumental defects. They are serious in the existing model of the refractometer, but could be got rid of almost entirely by proper design and workmanship.

Sources of Error in Using the Instrument.—The important points to receive attention in making a test are the fitting of the glass specimen on the block of the instrument, and the proper adjustment of the source of light. With regard to the former, it is clearly essential in order that refraction may be regarded as taking place at a single surface separating the specimen from the block, that the film of liquid used to give optical contact should have parallel sides.

This, of course, is generally realised, and the specimen is usually adjusted until the interface appears all of one interference colour when viewed by white light from a lamp suitably placed, or until only a few fringes *running parallel to the plane of refraction* are seen. Slight want of parallelism in a direction transverse to the plane of refraction will have a negligible effect on the angle of refraction since the deviation is in the neighbourhood of a minimum with respect to this adjustment. Any want of parallelism in a direction parallel to the plane of refraction gives rise to serious errors, except in the case of glasses of index quite near that of the α-mono-bromnaphthaline usually employed for the liquid film. In the case of glasses of low index, such as boro-silicate crowns, hard crowns, &c., the position of the critical edge is very sensitive to errors of parallelism in the film.

It is nevertheless possible to make the adjustment with the necessary accuracy ; but it is important to note that it is by no means certain to remain correct throughout the test of a specimen. A slight settling of the specimen, produced or aggravated by any vibration such as that caused by the interrupter of the induction coil, may be sufficient to cause several transverse fringes to develop at the interface during the measurements. The disposition of the fringes should always be examined after a test to detect any shift that may have occurred ; or alternatively the first line measured may be repeated at the end.

In either case if shift is detected it is necessary to re-adjust the specimen and repeat all observations. The possibility of such a shift may be reduced by using a very small drop of the liquid and squeezing most of it out in working the surfaces together Unfortunately this accelerates considerably the rate of deterioration of the block due to scratches on the surface, and it is necessary to compromise somewhat in the quantity of liquid employed.

A method of minimising this difficulty is to use a liquid with index only a little greater than that of the glass under test. It can be shown (*see* later, p. 174) that the error which will be made in measuring an index μ_1 with a liquid film of index μ_2

and angle θ seconds is $\frac{\theta\mu_2}{2\cdot06}\sqrt{1-\left(\frac{\mu_1}{\mu_2}\right)^2}$ units in the fifth place. The index of α-monobrom-naphthalene is 1·66, so that in measuring a glass of index 1·52, the error for each second of film angle is $\frac{1\cdot66}{2\cdot06}\sqrt{1-\left(\frac{1\cdot52}{1\cdot66}\right)^2}=0\cdot3$ units, *i.e.*, to throw the result out by 0·00001 a film angle of 3 seconds is required. The interference fringes are usually viewed fairly obliquely; so, allowing for this and for the index of the film, an angle of 3 seconds would correspond to about two or three transverse fringes in an interface of 15 mm.

The effect of film angle will clearly be reduced the more nearly μ_2 equals μ_1. To obtain a serious advantage, however, the approximation must be fairly close, because of the way in which the square root term varies with μ_2. Thus for $\mu_2=1\cdot55$ instead of 1·66 the error for a given angle of film is only halved. To reduce it to a quarter, μ_2 must be reduced to a little under 1·53, which is very close to the index of the glass. On the other hand, if μ_2 is too close to μ_1 there is a greatly increased difficulty in seeing the fringes owing to the small amount of reflection at the μ_1—μ_2 surface.

Liquids that prove satisfactory in use with the usual types of glass are :—

(*a*) For Borosilicate Crowns and Hard Crowns :—oil of cloves, oil of sassafras.
(*b*) For Baryta Light Flints :—nitro-benzol, oil of aniseed.
(*c*) For Medium Barium Crowns :—α-monobrom-naphthalene diluted with xylol (proportions may be readily found by trial).
(*d*) For Heavy Flints :—α-monobrom-naphthalene.

A further advantage of using a liquid with an index near that of the glass under test is that it minimises somewhat the defects of focus and definition due to imperfect planeness of the surface of the specimen.

Another matter requiring reasonable care is the adjustment of the source of light. It is sometimes possible to get a spurious sharp edge in the field of view which is sensibly displaced from the proper critical edge. At other times difficulty is experienced in getting a sharp edge at all. The only sure guide to the proper adjustment of the vacuum tube and condensing lens is experience.

Another source of uncertain readings is chromatic parallax. This chiefly affects the blue end of the spectrum. Its cause and cure are discussed in a previous Paper by the author* and need not be gone into in detail here. It was there stated that part of this effect is due to light scattered by the matt surface surrounding the polished horizontal face. This could be greatly reduced by polishing the curved surface as well as the plane. Another suggestion for the elimination of chromatic parallax in this instrument involves the use of a different type of graticule from that usually fitted. The new graticule consists of two vertical lines separated by such a distance that they subtend about seven-tenths of a minute at the centre of the object-glass. These lines are parallel to the edges of the coloured bands at the centre of the field. The setting is made by bringing the bifilar completely on to the coloured band and adjusting until the space between the edge and the wire most remote from it is bisected by the other wire. The wires being illuminated directly by the light of the band, chromatic parallax will not make itself evident unless the proportion of scattered light in the field is very strong. With this setting we are further freed from the difficulty, sometimes strongly felt with the ordinary cross-lines, that if the field is free from scattered light the part of the lines which are on the dark side of the edge are not always seen sufficiently well for proper settings to be made. There is one unfortunate drawback associated with this type of graticule, and that is that it cannot always be employed with the sodium line. There is a point to be observed in making measurements with sodium light on the Pulfrich refractometer that is not generally realised. In the first place one would hesitate to mention the obvious fact that the critical edge in the case of sodium light corresponds to the D_1 line,† but for the prevalent habit of assuming that it is the mean index for D_1 and D_2 that is given. Thus the tables issued by Zeiss and Hilger are stated to apply to the mean of the sodium lines instead of to D_1, as they ought to be.

For some specimens the instrument does not resolve the D lines, but in many cases they are resolved and can be seen as separate bands if the width of the bands is cut down sufficiently by means of a suitable shutter. When comparatively broad overlapping bands are employed, as in the ordinary use of the instrument, only a single band is seen, which is of double brightness except for the region near the edge where the light is due to D_1 alone. One does not, however, see the two edges; the eye simply averages them up as a single band with a soft instead of a sharply defined edge. When crosslines are set on an edge of this character the eye appears to accept as the edge the region where the intensity is falling off most rapidly, and the setting is made on a point inside the true edge of the outer component by an amount which seems to vary considerably with different individuals. Thus if one carefully sets the crosslines on the edge of the sodium band when it is broad (in the case of a specimen which can resolve the lines) and then gradually cuts down the width of the band, the setting will remain apparently correct until the bands are nearly resolved. The edge will then appear to move relative to the crosslines until, when the two components are completely resolved, it will be seen that the cross-lines are quite away from D_1. In many cases they will be much nearer D_2. As mentioned already, the setting is liable to relatively large variation of personal error, and so cannot be allowed for in the form of a correction. The only way to make satisfactory measurements with sodium is to cut down the width of the band until the components are resolved if it is possible to resolve them.* This, of course, prevents the use with this line of the bifilar graticule, which requires an appreciable width of band. To overcome this difficulty a compound graticule consisting of the ordinary diagonal cross-lines in addition to the bifilar was devised, Fig. 1. The two sets of lines are fairly close, so that neither is far from the centre of the field of view. The actual dimensions suggested for a focal length of $4\frac{1}{2}$ inches as the result of experiments with different graticules were: separation of components of bifilar = 0·025 mm.; distance $AB = 0{\cdot}25$ mm.*

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* Proc. Phys. Soc., Vol. XXIV., p. 330, *et seq.*

† Except in the rare cases when the dispersion of the substance under test is greater than that of the block in which case it is the D_2 line that gives the critical edge.

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* This will not be found to be at all a convenient process if the sodium light is obtained from a flame. In the first place the bands from a flame when cut down fine are very faint, and in the second place owing to the absence of background the cross-wires cannot be seen. For this reason the author prefers to obtain the sodium light from the vacuum tube used for the hydrogen lines, running it for the purpose at a pressure of about 3–5 cm. of Hg. This gives an intense sodium band when it has been running for a short time with a heavy discharge. The width of the band can then be controlled by means of the shutter in front of the condensing lens, while the necessary background for rendering the crosswires visible is supplied by the secondary hydrogen spectrum. Since the observations on the hydrogen lines themselves require exhaustion to about 1 mm. or less, somewhat special apparatus is necessary. The apparatus now used at the Laboratory was shown at the Optical Society's Exhibition on Jan. 11, 1917, and is described in the "Transactions" of the Optical Society, Vol. XVIII., 1917, pp. 22S and 23S.

In use, the bifilar setting would be employed for the G' line, for which it is primarily intended, and probably also for F and C; although for these lines it would not likely possess any marked advantages over the other. The ordinary cross would be employed for the sodium lines and for the zero reading, the constant difference between the two settings being determined once and for all on some line such as F, which is suited to both.

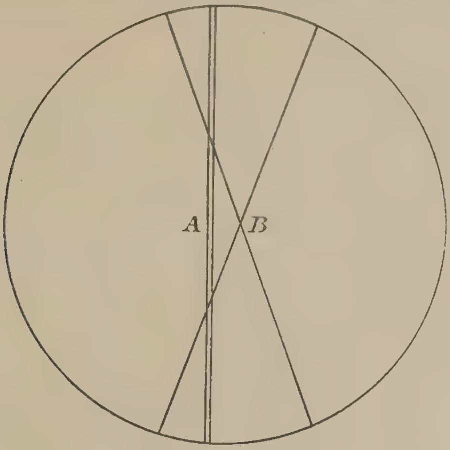

Fig. 1.—Compound Graticule (*not* to scale).

§ 4. Systematic Errors.

Centering Error.—There is no ready means of testing the circle of the ordinary Pulfrich refractometer for centering error. If this is present, as it is almost certain to be to a greater or less extent, incorrect angles of emergence will be obtained. A second vernier diametrically opposite to the first should be fitted, so that by taking the mean of their readings centering error may be eliminated.

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* This graticule is described in the present paper with the distinct reservation that it has not yet been possible to experiment with it under the actual conditions of illumination, definition, etc., of the refractometer. The experiments from which these dimensions were deduced were made on an ordinary spectrometer, the type of setting being imitated as closely as possible. The refractometer itself is usually so fully employed that the fitting of experimental graticules has not so far been feasible.

Unfortunately the methods by which centering errors can be measured when only one vernier is provided are not such as are usually available except in specially equipped laboratories. Of course, imperfect centering of the circle will not affect the dispersions measured on the micrometer screw. This error is therefore confined to the absolute values of the indices.

Micrometer Errors.--The micrometer screw readings give quantities proportional to the tangent of the angle between any position of the radius bar and its position when the plane of the polished steel surface against which the point of the micrometer bears is perpendicular to the axis of the latter.

The curve (Fig. 2*a*) gives the correction that has to be applied to the micrometer readings to give true angles. The case taken is that in which the position of the bar when the micrometer reads zero is 2° behind its position when the bearing plane is perpendicular to the screw.

The Pulfrich instrument is usually marked off for a range of 5° ; but the figure shows that the difference between tangent and angle is too big to be neglected beyond about 3°. It is convenient for glass testing to mark off an extra 2°, so as to increase the range to 7°. The correction becomes rapidly large at these angles.

There is a further source of error which may arise in the micrometer readings, and which may easily be more serious than those due to taking the tangents for the angles. The point involved, though well known to the makers of astronomical instruments for example, does not appear in all cases to receive the attention that it should where tangent screws are utilised as micrometers ; and it may be worth while on that account to indicate the nature and magnitude of the effect.

Suppose we have a radius bar CD (Fig. 3*a*) rotating about a centre C and actuated by a micrometer screw of which the axis is in the direction AB. Let $P'Q'$ be the plane of the bearing surface and Cb' the plane through C parallel to it. Let the position of the bar when the micrometer reads zero be as shown, in which it makes an angle θ_0 with the position in which the bearing plane is perpendicular to the screw.

Suppose the screw is now advanced until the perpendicular position is reached. The micrometer registers the length aa', corresponding to an angle (taking tangents for angles) of $\frac{aa'}{Cb}$.

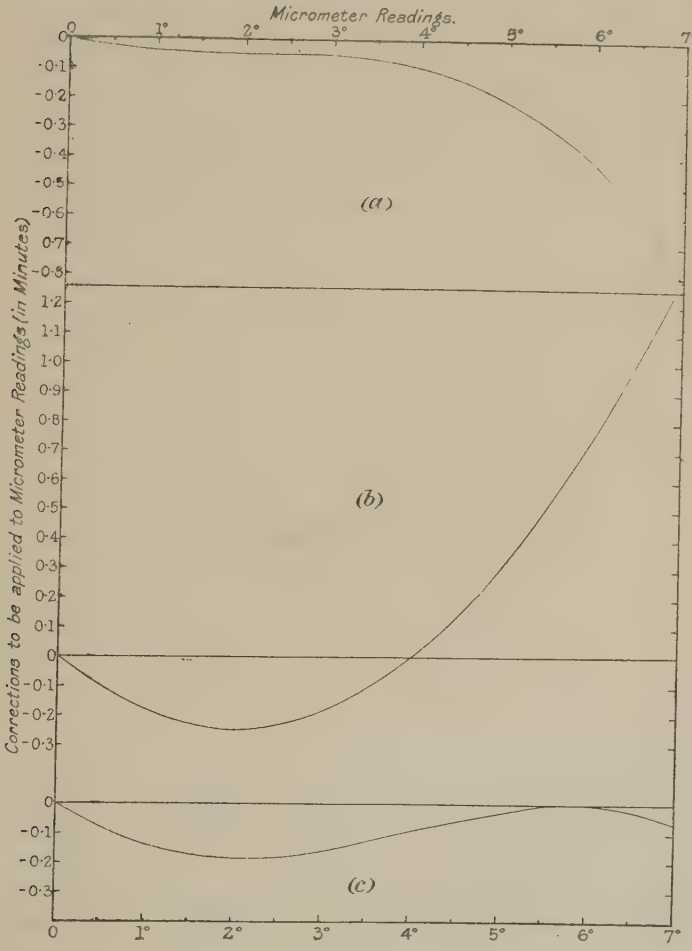

FIG. 2.

The actual angle through which the bar has rotated is $\frac{bb'}{Cb}$. The micrometer reading, therefore, exceeds the true angle by

$$(a'a-b'b)/Cb=(a'b'-ab)/Cb=\frac{ab}{Cb}(\sec\theta_0-1).$$

Thus a correction of $-\frac{p}{r}(\sec\theta_0-1)$ has to be applied to the micrometer reading to give the true angle, p being put for the perpendicular distance from the centre to the bearing plane and r for the perpendicular from the centre to the micrometer axis. It is easy to see that in general for any angle θ measured from the zero of the micrometer, the correction to be applied is

$$-\frac{p}{r}\{\sec\theta_0-\sec(\theta-\theta_0)\}.$$

We see from this expression that as we proceed along the micrometer, a negative correction has to be applied which reaches a maximum value when $\theta=\theta_0$, and then diminishes to zero when $\theta=2\theta_0$, thereafter becoming positive and increasing rapidly. Fig. 2*b* shows this correction curve when $p=1$ cm. and $r=8{\cdot}5$ cm.; θ_0 is again taken as 2°.

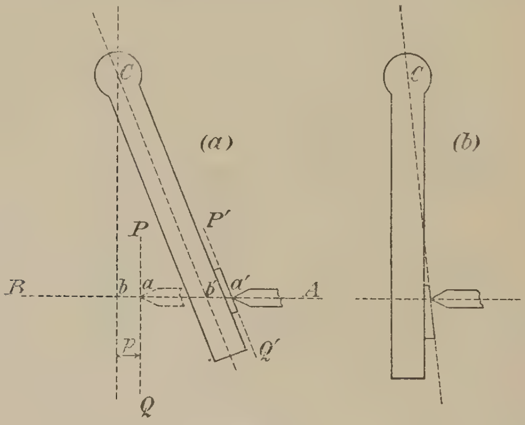

FIG. 3.

In order that this correction should disappear it is necessary that p should be zero, *i.e.*, the bearing plane should pass through the centre C, Fig. 3 (*b*).

This point has been given no attention in the Zeiss refractometer. In the specimen at the Laboratory the bearing plane instead of sloping so as to pass through the centre as in Fig. 3 (*b*) actually slopes away from it, the result being a large value of p. Fig. 4 shows the *total* correction curve which has to be applied to the micrometer readings of this instrument. Since this includes the tangent corrections corresponding to Fig. 2(*a*) as well as the error under discussion, to get the curve for this error alone we have to raise curve 4 by the ordinates of a curve similar to Fig. 2(*a*). When we see that this error, which ought to be zero throughout, reaches nearly 2 minutes at 7°.

Unfortunately it is not easy to determine the curve of correction to a micrometer screw in the absence of special apparatus. One method by which it can be carried out on the instrument itself is to clamp the radius bar to the circle in such a position that when the micrometer reads zero there is an approximate coincidence between the zero of the vernier and a scale division on the circle. The coincidence is then made accurately by means of the tangent screw, and the micrometer reading noted. The screw is then advanced until the next scale division is opposite the vernier zero and so on. In this way a series of micrometer readings corresponding to every half degree is obtained. The measurements must be repeated at several different parts of the circle to average out irregularities in the circle graduations. If these graduations were of satisfactory fineness this would be a comparatively good method of calibrating the micrometer, provided, of course, that the patience in repetition which is essential to all standardisation methods is applied. With the Zeiss instruments, however, owing to the poor quality of the dividing the error of a single observation is so great that the amount of repetition

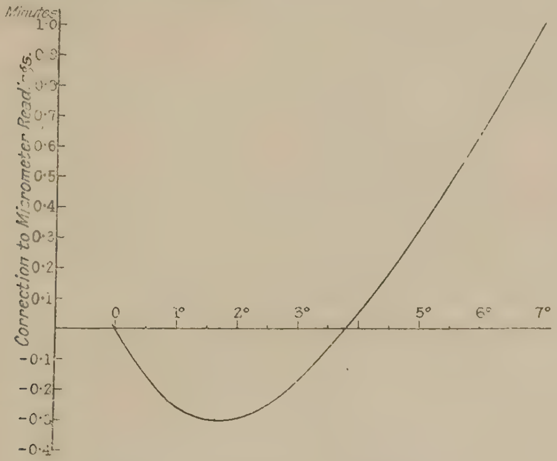

Fig. 4.—Pulfrich Refractometer.
Total correction curve to an actual micrometer.

required to get satisfactory results is excessive, and one would not use the method except where others are not available.

But although this method would not be employed in a standardising institution, it certainly gives the user of the instrument a means, even if it is a tedious one, of determining this important correction which is absolutely vital to dispersion measurements. It will sometimes be found that in calibrating the screw it is impossible to get successive calibrations to agree satisfactorily. Irregularities of this kind are often traceable to the vernier rubbing on the edge of the circle. If the vernier is set back sufficiently to allow perfectly free motion of the circle the discrepancies will probably disappear.

Figs. 2 (*b*) and 4 show that if there is excess of the error due to the cause just discussed—which we may call the p error for short—the correction curve will be very steep at the higher angles. In the event of the p error being entirely absent, Fig. 2 (*a*) shows that the correction curve, which is in this case simply due to the tangent error, also becomes steep at the higher angles. Now a steep correction curve is always difficult to determine accurately, and is also more liable to be misread in use. It is, therefore, better to introduce intentionally a suitable amount of p error to produce partial compensation of the tangent error. Complete compensation is clearly impossible because of the dissimilar shapes of curves 2 (*a*) and 2 (*b*), but a residual correction curve may be obtained which is nowhere steep or of large amplitude. In Fig. 2 (*c*) is plotted the resultant correction curve obtained by introducing sufficient p error to neutralise the tangent error at 6° from the zero of the micrometer. The value of p/r required when $\theta_0=2°$ is 0·067. This gives a much more satisfactory correction curve over the 7° range than Fig. 2 (*a*) alone. A flat curve like this could then be compensated completely by suitably shaping the edge of the plate against which the drum is read as in Fig. 5.

Before leaving this question it may just be mentioned that if p is of opposite sign to the cases considered here, *i.e.*, if the plane of the bearing surface passes the centre on the side remote from the micrometer the resulting errors will be of opposite sign to those of Fig. 2 (*b*). This, however, is not likely to be so frequently met with as the other case.

Filling the Aperture.—The next point to be considered in connection with possible systematic error is the manner in which the beam of light enters the telescope. The refracted light all comes from the circular horizontal face of the block. Owing to the obliquity produced by the two refractions, the section of the beam when it reaches the telescope is a somewhat narrow ellipse of which the minor axis is parallel to the plane of refraction, and is the effective aperture of the beam in this plane. The effective aperture is zero for angles of emergence from the second face of the block ot 0 or 90°, and has a maximum value of roughly one-third the diameter of the interface at an intermediate angle. The telescope is fitted with an elliptical stop in front of the object-glass, which is intended to be just about the size of the maximum aperture

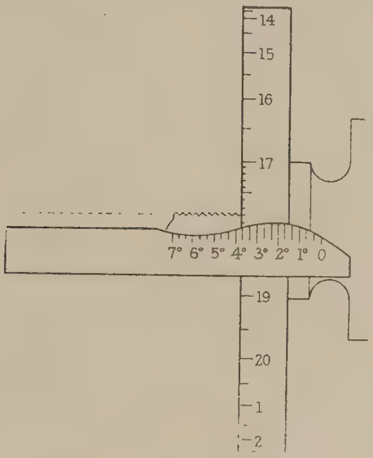

Fig. 5. (About twice full size.)

of the beam, but is usually a bit larger. Now the pencil of light which enters the telescope can only be symmetrical with the optic axis if the central ray of the beam passes through the centre of the stop or else if the width of the beam is sufficiently in excess of the width of the stop to ensure that the latter is completely filled.

From the nature of the case it is impossible for the central ray of the emergent beam to pass centrally through the stop for all angles of emergence, because these central rays, produced backwards, do not radiate from any single point.

There is thus no point at which the centre of rotation can be situated, such that the axis of the telescope can be brought into *coincidence* with the central ray of the emergent beam for all angles of emergence.

The only method of ensuring that a symmetrical portion of the objective is used is to increase the diameter of the circular face of the block so that the width of the emergent beam is sufficiently in excess of the aperture of the telescope to fill it at all angles within the practical range.

In the ordinary refractometer this is never the case. When the telescope is set on a spectrum line, if the exit pupil be examined with a magnifier the elliptical section of the light beam and its relation to the stop can be easily seen. The illuminated ellipse will usually be smaller than the stop and will probably lie towards one side of it.

When the central ray of the beam which enters the telescope does not pass through the centre of the objective, errors will arise in the measured position of the image unless the focal plane coincides exactly with the plane of the cross-lines. There is a variety of causes from which slightly incorrect focus may arise in practice. In the first place the adjustment may not be quite correct for any wave-length, while it certainly can not be correct for all wave-lengths with the ordinary doublet lens employed. Also slight defects of planeness of the surface of the specimen under test appreciably affects the focus. Thus to be quite safe from error the aperture must be fully or at least symmetrically filled with light. If such errors are present they may enter into the dispersion measurements, since the focal defects are not necessarily the same for all wave-lengths.

Fortunately in existing refractometers it is usually possible to make the beam symmetrical with the stop by adjusting the height of the block on the pillar while examining the exit pupil. Every time this is done the condenser and source of light must be adjusted to suit.

Adjustment of Telescope and Block.—It is essential that the axis of the telescope should be perpendicular to the axis of rotation, and also that the refracting edge of the block should be parallel to the axis of rotation. The former adjustment can be very easily verified by removing the block and resting on the top of the pillar a strip of brass to which a piece of plane glass has been fixed, approximately at right angles, by means of wax or plasticene. The telescope is then brought up until the autocollimated image from the front face is in the field, and the brass plate is then adjusted by hand in the horizontal plane until exact coincidence can be obtained. The telescope is then rotated through 180°, so as to obtain the image reflected from the back of the glass. If the adjustment of the axis is correct exact coincidence can be obtained without altering the position of the plate. If, however, the image is nearer to or further from the centre of the field than it should be, half the defect must be remedied by altering the adjustment of the glass and half by the adjustment of the telescope. Unfortunately there is no proper provision for this adjustment, so that if any is really necessary it must be done by packing under the flange with thin tin foil.

When the telescope is correctly fitted the block should give normal reflection from each of the faces. The adjustment of the vertical face is usually left just a little bit out to give a better type of setting for the zero readings. This degree of incorrect adjustment is, of course, negligible, but the adjustment of the horizontal face is frequently found to require improvement. There is no adjustment provided for this, and here again packing must be resorted to if necessary.

Optical and Geometrical Properties of Block.—The final direction of the emergent beam depends on the refractive index of the block and also on its angle; and it is not generally found that either of these constants is sufficiently near the values adopted in computing the tables for use with the instrument. It is necessary to check both the index of the block and the angle, and to apply corrections if these differ from their nominal values.

The determination of the index of the block can only be performed by determining the angles of emergence when a specimen of known properties is placed on it. It is obvious at the outset that to accomplish this calibration efficiently is a matter of some difficulty. The requirements as to a standard substance are very severe. If a glass specimen is employed it must be one of which the indices have been determined by an absolute method to a certain accuracy of 1 in the fifth decimal place. This requires a spectrometer outfit of the highest precision, and there are very few laboratories in which equipment nearly good enough for the purpose is available. The alternative is to use some substance such as quartz, for which accurate data have been obtained by various experimenters. Unfortunately, when the available data for quartz is consulted very considerable differences between the results of different observers are found. Some do not specify whether right or left handed quartz is referred to, although there appears to be an appreciable difference between their refractive properties. It is somewhat difficult, therefore, to decide what weight to give to different determinations. The values provisionally adopted at the laboratory for the ordinary ray are :—

$$n_C=1{\cdot}54187,\ \ n_{D_1}=1{\cdot}54421,\ \ n_F=1{\cdot}54966,\ \ n_{G'}=1{\cdot}55394,$$

based on the results of Martens, Gifford, Müller, van der Willigen, Macé de Lépinay, Dufet, Sarasin, Quincke and Mascart.

These are only accepted, however, pending the completion of experiments that are in progress. At present the author inclines to the belief that variations of several units in the fifth place may be found in the indices of specimens of quartz obtained from different localities. This might explain the difference between Col. Gifford's figures and those of most other observers.

Much closer agreement is to be found among the various determinations for distilled water ; but the high temperature coefficient of liquids and also the fact that water cannot be used with the denser blocks renders this substance unsuitable for standardisation purposes.

We are thus faced at the outset with considerable difficulty in obtaining a standard substance with sufficiently well-established constants to give the requisite accuracy in the constants of the block.

In order to overcome this difficulty the author has suggested the use of blocks with smaller angles than the customary 90°. It is clear that if the angle of the block is less than $2\sin^{-1}\frac{1}{\mu}$, where μ is its refractive index, there will be an emergent beam corresponding to light entering the top surface at grazing incidence in air, and the index of the block can be measured directly on the instrument without reference to any intermediate standard substance.

§ 5. THE GENERAL CRITICAL ANGLE METHOD.

In order to understand fully the advantages or otherwise associated with this departure it is desirable to examine in detail the problem of refraction by a system such as we have in the Pulfrich refractometer.

Suppose we have a prism of index μ_2 and angle θ separating two media of μ_1 and μ_3. Let AB, Fig. 6, be a ray of light incident at grazing incidence on the first face of the prism, BCD being its subsequent path. The author finds it convenient in refraction problems to adopt the usual convention that all angles are positive when measured counter-clockwise from the appropriate reference lines. For rays of light the reference lines are the normals at the points of incidence or emergence as the case may be, while for prism angles, the normal to the surface first encountered is taken as the reference line with respect to which the direction of the other normal is defined. In Fig. 6 all the angles are positive on this convention. Taking the signs of the angles into account in this way has the disadvantage that some of the usual formulæ of refraction by prisms have the signs of certain quantities reversed ; but it has the much greater advantage of preventing confusion in many practical cases in which doubt as to sign may arise if one considers only the magnitude of the angles as is usually done in evolving prism formulæ.

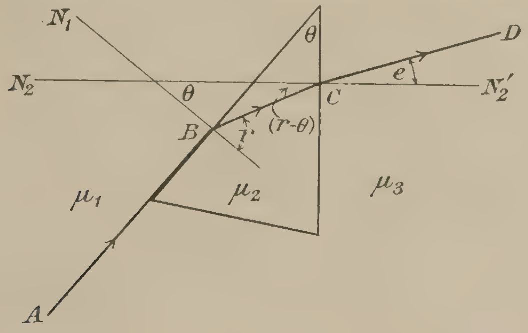

FIG. 6.

Applying the laws of refraction to the two surfaces, we have

$$\frac{\sin(r-\theta)}{\sin e}=\frac{\mu_3}{\mu_2} \text{ and } \frac{\mu_1}{\mu_2}=\sin r,$$

$$=\sin\{\theta+(r-\theta)\},$$

$$=\sin\theta\cos(r-\theta)+\cos\theta\sin(r-\theta),$$

$$=\sin\theta\sqrt{1-\left(\frac{\mu_3}{\mu_2}\right)^2\sin^2 e}+\cos\theta\frac{\mu_3}{\mu_2}\sin e,$$

whence $$\frac{\mu_1}{\mu_3}=\sin\theta\sqrt{\left(\frac{\mu_2}{\mu_3}\right)^2-\sin^2 e}+\cos\theta\sin e \quad . \quad (1)$$

Before applying this to the Pulfrich system as a whole we may consider it as applying to the three media—specimen, liquid film, block; in which case μ_1 is the index of the specimen, μ_2 that of the liquid film, θ the angle of the film, and e the angle of refraction *into* the block.

If the adjustment of the film is correct so that $\theta=0$

$$\sin e=\mu_1/\mu_3,$$

as in the theoretical case with no film present. If, however, the adjustment is imperfect, this will not be the case. Equation 1 becomes for very small values of θ

$$\frac{\mu_1}{\mu_3}=\theta\sqrt{\left(\frac{\mu_2}{\mu_3}\right)^2-\sin^2 e}+\sin e(1-\tfrac{1}{2}\theta^2)$$

$$\sin e=\frac{\mu_1}{\mu_3}-\theta\sqrt{\left(\frac{\mu_2}{\mu_3}\right)^2-\left(\frac{\mu_1}{\mu_3}\right)^2},$$

neglecting terms involving higher powers of θ than the first.

Whence $$\mu_3 \sin e=\mu_1-\mu_2\theta\sqrt{1-\left(\frac{\mu_1}{\mu_2}\right)^2}.$$

Now, for a given direction of the emergent beam we would deduce a value μ_1' for μ_1, such that $\mu_1'=\mu_3 \sin e$; so that the error

$$\mu_1-\mu_1'=\mu_2\theta\sqrt{1-\left(\frac{\mu_1}{\mu_2}\right)^2}=\mu_2\frac{\theta}{2\cdot 06}\sqrt{1-\left(\frac{\mu_1}{\mu_2}\right)^2},$$

where $\mu_1-\mu_1'$ is measured in units in the fifth decimal place and θ is in seconds of arc.

In considering refraction by the whole system we neglect the film and take μ_2 in equation 1 as the index of the block and θ its angle. μ_3 is then the index of air and may be put $=1$. The equation then becomes

$$\mu_1=\sin\theta\sqrt{\mu_2^2-\sin^2 e}+\sin e\cos\theta, \quad . \quad . \quad . \quad (2)$$

which is the relation connecting the index of the specimen (μ_1) with the index and angle of the block and the angle (e) of emergence from the last surface in the general critical angle method.

It should be noted in applying the formula to particular examples that e is positive if the emergent ray is on the same side of the normal as the refracting edge, and is negative if it is on the side of the normal remote from the edge.

In the particular case in which $\theta=90°$, $\mu_1^2=\mu_2^2-\sin^2 e$, which is the relation for the ordinary Pulfrich refractometer.

If we differentiate the right-hand side of equation 2 with respect to e, θ and μ_2 being constant, we find

$$\frac{\partial\mu_1}{\partial e}=\frac{1}{2}\,\frac{\sin\theta}{\sqrt{\mu_2^2-\sin^2 e}}(-2\sin e\cos e)+\cos e\cos\theta$$

$$=\frac{\cos e}{\sqrt{\mu_2^2-\sin^2 e}}\left\{\cos\theta\sqrt{\mu_2^2-\sin^2 e}-\sin e\sin\theta\right\},$$

which, after transformation and substitution from equation 2, reduces to

$$\frac{\cos e}{\sqrt{\mu_2^2-\sin^2 e}}\sqrt{\mu_2^2-\mu_1^2}.$$

The inverse of this quantity, $\frac{\partial e}{\partial\mu_1}$, measures the sensitivity of the measurements. It is convenient to express sensitivities in terms of seconds of arc per 0·00001 change in μ_1. Calling this quantity S_{μ_1},

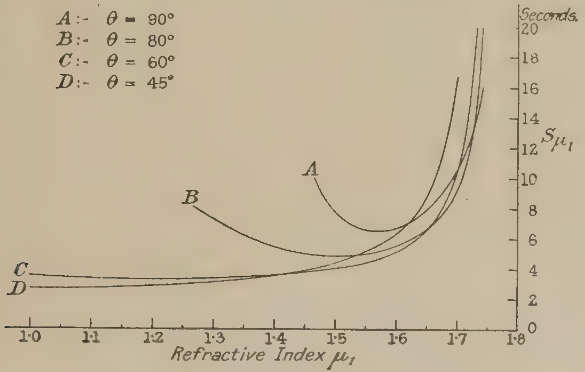

FIG. 7.—PULFRICH REFRACTOMETER.
Sensitivity curves for blocks of different angles.

$$S_{\mu_1}=2{\cdot}06\frac{\partial e}{\partial\mu_1}=\frac{2{\cdot}06\sqrt{\mu_2^2-\sin^2 e}}{\cos e\sqrt{\mu_2^2-\mu_1^2}}\quad . \quad . \quad . \quad . \quad (3)$$

For any value of μ_2, S_{μ_1} can be calculated for various values of μ_1 for any prism angle, the corresponding value of e being found from equation 2.*

In Fig. 7 a series of curves are drawn showing for the case

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* Equation 2 is in its most convenient form for deducing μ_1 from known values of e and θ. For the inverse process of deducing the value of e corresponding to a given μ_1 it can be reduced to the form

$$\sin e=\mu_1\cos\theta-\sin\theta\sqrt{\mu_2^2-\mu_1^2}.$$

in which $\mu_2=1{\cdot}75$ (a usual value) how the sensitivity varies with the index under test (μ_1) for blocks of different angles. The sensitivity is in all cases high for indices near that of the block, diminishing to a minimum value which is lower, and occurs at a lower value of μ_1 the smaller the angle.

Thus with a 90° angle the minimum occurs at $\mu_1=1{\cdot}57$ approx. and is about 6 seconds: for $\theta=80°$ the minimum is at $\mu_1=1{\cdot}5$ and is under 5 seconds; for $\theta=60°$ the minimum is not reached until μ_1 is in the neighbourhood of 1·2 and is just over 3 seconds, while for $\theta=45°$ the minimum is never reached. These results will be discussed later in conjunction with others.

Effect of Error in θ.—If an erroneous value is assumed for the angle of the block, the corresponding error in the calculated value of μ_1 will be proportional to the partial differential of equation 2 with respect to θ.

$$\frac{\partial\mu_1}{\partial\theta}=\cos\theta\sqrt{\mu_2^2-\sin^2 e}-\sin e\sin\theta,$$

which reduces to $\sqrt{\mu_2^2-\mu_1^2}$.

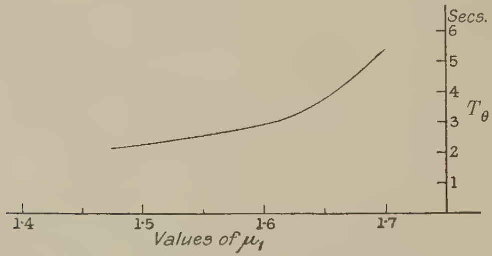

FIG. 8.—PULFRICH REFRACTOMETER.
Error in angle of block which will cause error of 0·00001 in μ_1. $\mu_2=1{\cdot}75$.

If we denote by T_θ (which we may call the tolerance in prism angle) the error in θ, measured in seconds, which will throw out the value of μ_1 by 0·00001, we may write

$$T_\theta=2{\cdot}06\frac{\partial\theta}{\partial\mu_1},$$
$$=\frac{2{\cdot}06}{\sqrt{\mu_2^2-\mu_1^2}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This is always positive, so that if the assumed value of θ is too large, the deduced value of μ_1 will be too large and vice versa. Also we see that T_θ is independent of the angle of the block, *i.e.*, the error in θ which will affect μ_1 by a given amount is independent of the shape of the block.

In Fig. 8 the way in which the tolerance varies with the index under test is shown. We see from it that the effect of an error in the angle of the prism diminishes the higher the index under test.

For the lightest glasses ($\mu_1=1{\cdot}5$) an error of 2 seconds in the angle of the block will throw out the index by one unit. While even if we confine the use of this block ($\mu_2=1{\cdot}75$) to glasses of 1·6 and over, as would usually be done in practice, the value of T_θ is only 3 seconds. It is thus clearly necessary that the measurements of the angle of the block should be made with the utmost accuracy.

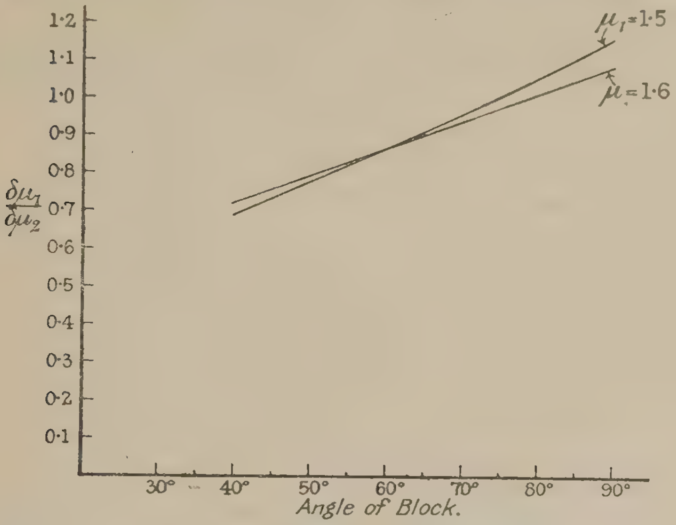

FIG. 9.—PULFRICH REFRACTOMETER.

$\frac{\partial\mu_1}{\partial\mu_2}$ for different angles of block. $\mu_2=1{\cdot}75$.

Effect of Error in μ_2.—If an erroneous value is assumed for μ_2, the index of the block, the error produced will be proportional to $\frac{\partial\mu_1}{\partial\mu_2}$.

$$\frac{\partial\mu_1}{\partial\mu_2}=\frac{\mu_2\sin\theta}{\sqrt{\mu_2{}^2-\sin^2 e}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In the case of the ordinary Pulfrich instrument this reduces to μ_2/μ_1.

In Fig. 9 the value of $\partial\mu_1/\partial\mu_2$ is shown for different block angles for two values of μ_1. The effect of an error in μ_2 diminishes as the angle of the block is diminished.

Measurement of μ_2 with Air as Standard.—Before discussing the foregoing results, let us consider the method of calibrating the block without an auxiliary standard substance. As mentioned already, the largest angle with which this would be possible is $2\sin^{-1}\frac{1}{\mu_2}$, which for $\mu_2=1{\cdot}75$ is about $69\frac{3}{4}°$, while for the lower index 1·6 it is about $77\frac{1}{3}°$.

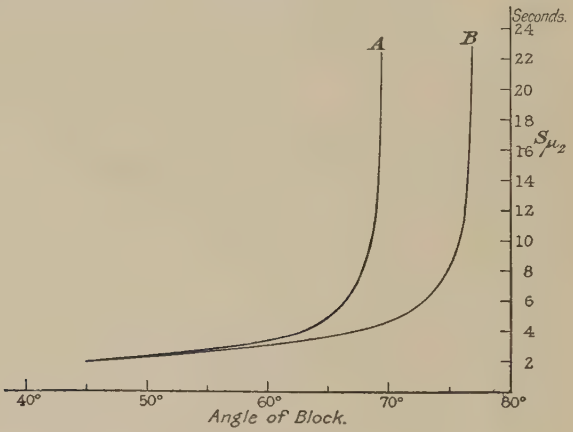

FIG. 10.

S_{μ_2}=number of seconds change in emergent angle for change of 0·00001 in μ_2 while measuring μ_2 with air as standard substance.

A : $\mu_2=1{\cdot}75$. *B* : $\mu_2=1{\cdot}6$.

If $\mu_1=1$, equation 2 may be reduced to

$$\mu_2^2=1+\left(\frac{\cos\theta-\sin e}{\sin\theta}\right)^2, \quad . \quad . \quad . \quad . \quad (6)$$

a form suitable for calculating μ_2 from observed values of e, or

$$\sin e=\cos\theta-\sin\theta\sqrt{\mu_2^2-1} \quad , \quad . \quad . \quad . \quad (6a)$$

which is more convenient for calculating the angle of emergence for a given value of the index of the prism.

The sensitivity of this method may be denoted by S_{μ_2} and is obviously, in the same units as before, given by

$$S_{\mu_2}=2{\cdot}06\,\frac{\partial e}{\partial\mu_2}.$$

Differentiating equation 6

$$2\mu_2\frac{\partial\mu_2}{\partial e}=-2\left(\frac{\cos\theta-\sin e}{\sin\theta}\right)\frac{\cos e}{\sin\theta}=-2\sqrt{\mu_2^2-1}\,\frac{\cos e}{\sin\theta},$$

or

$$S_{\mu_2}=-\frac{2{\cdot}06\mu_2\sin\theta}{\cos e\sqrt{\mu_2^2-1}}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

S_{μ_2} is clearly always $-$ve, *i.e.*, the ray is always deviated further away from the refracting edge for an increase of μ_2. In Fig. 10 S_{μ_2} is shown for different angles in the cases of $\mu_2=1{\cdot}75$ and $\mu_2=1{\cdot}60$.

It is infinite for the maximum possible angle, decreasing with great rapidity as the angle is diminished by a few degrees, and then varying much less rapidly for still lower angles.

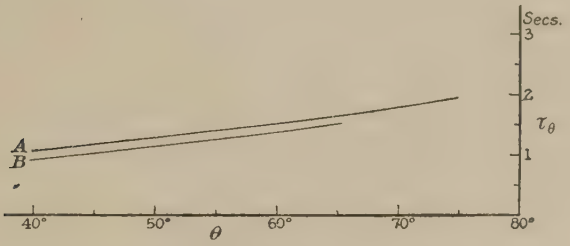

FIG. 11.

τ_θ=Error in angle of block which will produce error of 0·00001 in μ_2.

A : $\mu_2=1{\cdot}6$. B : $\mu_2=1{\cdot}75$.

Effect of Angle Error in Measuring μ_2.—From equation 6 we obtain

$$2\mu_2\frac{\partial\mu_2}{\partial\theta}=2\left(\frac{\cos\theta-\sin e}{\sin\theta}\right)\left[-\frac{\sin\theta}{\sin\theta}-\frac{(\cos\theta-\sin e)}{\sin^2\theta}\cos\theta\right]$$

$$=-2\sqrt{\mu_2^2-1}\left(1+\frac{\cos\theta}{\sin\theta}\sqrt{\mu_2^2-1}\right),$$

whence

$$\tau_\theta=2{\cdot}06\frac{\partial\theta}{\partial\mu_2}=\frac{-2{\cdot}06\mu_2}{\sqrt{\mu_2^2-1}+(\mu_2^2-1)\cot\theta}, \quad . \quad (8)$$

where τ_θ is the tolerance in angle for measurement of μ_2.

In Fig. 11 the variation of this function with θ for indices of 1·75 and 1·60 is shown. We see that the accuracy demanded in the measurement of the angle increases as the angle is diminished.

§ 6. DISCUSSION OF RESULTS.

We are now in a position to study the effect of varying the angle of the block on the general utility of the instrument. Referring in the first place to the sensitivity curves of Fig. 7, we see that owing to the way the curves intersect one another a block of any particular angle is less sensitive than one of a larger angle below a certain value of μ_1 and more sensitive above that value. Thus a 60° block is more sensitive than one of 80° if $\mu_1 > 1{\cdot}65$, and better than 90° if $\mu_1 > 1{\cdot}71$; while a 45° block is better than 60° above 1·425, *i.e.*, for all glasses, better than 80° above 1·54 and better than 90° above 1·62. The effect of errors in μ_2 (*see* Fig. 8) also diminishes the smaller the angle; while the effect of errors in the angle of the block was seen to be independent of the angle. These considerations point to the desirability of using as small an angle as possible.

If we now turn our attention to the problem of determining the index of the block, we find that high sensitivity can only be obtained in this measurement if the angle of the block is nearly the maximum possible (*see* Fig. 10). For the major portion of the practicable range of angle the sensitivity is fairly low and diminishes continuously as the angle is made less. Further, the effect of error in the angle on this measurement increases at lower angles (*see* Fig. 11). Thus from the point of view of accuracy in the standardisation of the block it is desirable to use as large an angle as possible. Moreover, the gain in sensitivity in standardisation which would be effected by choosing a value of θ well on the steep parts of the curves (Fig. 10) much more than outweighs the gain in sensitiveness given by a smaller angle in the measurements of μ_1, subsequently made with the block. We would therefore be led to employ for a given block as large an angle as possible consistent with the existence of an emergent beam when $\mu_1=1$.

There are, however, other considerations to be taken into account. If we use a value of θ just a little under $2\sin^{-1}\dfrac{1}{\mu_2}$, as suggested by these considerations alone, the aperture of the emergent beam when performing the standardisation measurements would be very small and the definition of the telescope would be very seriously impaired. Also the direction of the beam would pass so far from the centre of rotation of the telescope that it would be impossible to arrange the various parts of the instrument to be suitable for its ordinary use and for the standardisation measurements as well.

There is also the question of the measurement of the angle of the block. While it may be possible with a very accurate spectrometer to measure any angle to the desired accuracy—about 2 seconds—it is certainly a matter of the greatest difficulty in the general case. There are, however, comparatively simple methods whereby this accuracy can be obtained in the case of angles of 90°, 60° and 45°. This important limitation, therefore, reduces the choice of angles, other than 90°, to 60° and 45°. This being so, the balance of advantages undoubtedly lies with a 60° block, and we may now consider just what the requirements are in this case and the likelihood of their being satisfactorily realised. From Fig. 10, in the case of a 60° block, the sensitivity when measuring the index of the block is about 3 seconds per 0·00001. The probable error of a single observation is 0·1 minute, which therefore corresponds to 0·00002. In standardisation measurements a large series of observations ought always to be made, and no difficulty should be experienced in obtaining values correct to less than half the uncertainty of a single observation. The necessary accuracy in μ_2 is therefore quite possible provided, of course, that the mechanical accuracy of the instrument is sufficient.

With regard to error in the angle of the block, we find from Fig. 11 that an error of 1½ seconds will be sufficient to produce an error of 0·00001 in the value of μ_2; while in using the block for the measurement of other substances an error of 2 seconds (Fig. 8) will throw out the value of μ_1 by 0·00001 in the worst case ($\mu_1=1{\cdot}5$), provided the correct value of μ_2 is known. But if μ_2 is measured on the instrument itself the effect of a given error in angle on the values of μ_1 subsequently tested on the block will be reduced; for the values of $\frac{\partial\mu_1}{\partial\theta}$ and $\frac{\partial\mu_1}{\partial\mu_2}$ are always positive while the expression for $\frac{\partial\mu_2}{\partial\theta}$ is essentially negative. Thus if we assume too large a value for θ the value of μ_1 will also tend to be too large. But we shall have obtained a value for μ_2 in the standardisation measurement that is too low. This will tend to give a small value for μ_1, and will partially counteract the other effect. Since the errors are small we may treat them independently and add them. If $\delta\theta$ is the error in θ, the error in μ_2 on this account is $\left(\frac{\partial\mu_2}{\partial\theta}\right)\delta\theta$.* The error which this introduces in the subsequent measurement of an index μ_1 with the instrument is

$$\left(\frac{\partial\mu_1}{\partial\mu_2}\right)_2\delta\mu_2=\left(\frac{\partial\mu_1}{\partial\mu_2}\right)_2\left(\frac{\partial\mu_2}{\partial\theta}\right)_6\delta\theta,$$

and is negative if $\delta\theta$ is positive. The error in the opposite direction is $\left(\frac{\partial\mu_1}{\partial\theta}\right)_2\delta\theta$, the total error therefore being the algebraic sum, $\delta\mu_1=\delta\theta\left\{\left(\frac{\partial\mu_1}{\partial\theta}\right)_2+\left(\frac{\partial\mu_1}{\partial\mu_2}\right)_2\left(\frac{\partial\mu_2}{\partial\theta}\right)_6\right\}$,

or to express it in the form hitherto adopted,

$$\frac{\delta\theta}{\delta\mu_1}=\frac{1}{\left\{\left(\frac{\partial\mu_1}{\partial\theta}\right)_2+\left(\frac{\partial\mu_1}{\partial\mu_2}\right)_2\left(\frac{\partial\mu_2}{\partial\theta}\right)_6\right\}} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

When equation 9 is evaluated we find that the error in angle required to give a value of μ_1 which is too low by 0·00001 is $5\frac{1}{2}$ seconds for $\mu_1=1{\cdot}5$, $3\frac{1}{2}$ seconds for 1·6 and just under 3 seconds for 1·65. There should be no difficulty in determining the angle of the block to within this limit.

Thus the determination of the constants of the block by measurements independent of those made by the makers appears to be quite practicable if the block is cut to 60° instead of 90° as at present. The advantages of this do not require to be emphasised. Quite apart from the fact that individual blocks vary considerably in their properties from the representative samples tested by the makers, it is clearly undesirable that the accuracy of all subsequent work with the instrument should depend on the accuracy with which the initial determinations have been made, or that it should be impossible to check the maker's values except by reference to an intermediate standard, in view of the difficulties in connection with such standards mentioned earlier in the Paper.

A further important advantage of the 60° block is that the actual angles of emergence are in general smaller than in the case of 90° since the rays emerge more nearly normal to the second face. This greatly diminishes the possible effects of centering error or other circle deficiencies. In fact, over a limited range of index the emergent angles will be sufficiently small that both the dispersion measurements and the zero reading can be obtained on the micrometer, thus obviating in these special cases any reference to the circle at all. Specially simplified, but still accurate, refractometers might be constructed on these lines for use over a small range of index. The properties of the block being selected to give zero emergent angle for an index at the middle of the range, the measurements could all be made on a micrometer working over, say, 10°, no circle or clamping screws being required. Such an instrument might be very useful in certain industrial processes.

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* The suffix is the number of the expression from which the partial differential coefficient is obtained.

Reverting to the complete instrument the loss of sensitivity in the 60° case as compared with the 90° is slight over the range of indices required for glass testing, especially if a block of ordinary flint glass is used for the lightest glasses, as is the usual custom. But even using the denser block (1·75) with the lightest glasses, the sensitivity is still sufficient to give indices to the nearest unit in the fifth place if the settings are accurate to the nearest tenth of a minute.

In the calibration of the ordinary 90° block, by means of an auxiliary substance, the compensation of the effect of an error in θ on the measurements subsequently made with the instrument by the error, which is introduced in the value of μ_2 obtained in the standardisation, also holds. In fact, in this respect the auxiliary substance method of calibration is much superior to the other, because the effect of angle error is zero when measuring an index equal to that of the substance used for calibrating the block.

The equation which corresponds to equation 9 when the value of μ_2 is obtained by measurements of an auxiliary substance other than air is clearly

$$\frac{\delta\theta}{\delta\mu_1} = \frac{1}{\left\{\left(\frac{\partial\mu_1}{\partial\theta}\right)_2 + \left(\frac{\partial\mu_1}{\partial\mu_2}\right)_2 \left(\frac{\partial\mu_2}{\partial\theta}\right)_2\right\}} \quad . \quad . \quad . \quad . \quad (10)$$

In the case of a 90° block $\left(\frac{\partial\mu_1}{\partial\theta}\right)_2$ reduces to $-\sin e$ and $\left(\frac{\partial\mu_2}{\partial\theta}\right)_2$ is easily shown to be $\frac{\mu_1}{\mu_2}\sin e$, while $\left(\frac{\partial\mu_1}{\partial\mu_2}\right)_2 = \frac{\mu_2}{\mu_1}$.

Equation 10 then becomes, in seconds per 0·00001,

$$\frac{\delta\theta}{\delta\mu_1} = \frac{2{\cdot}06.}{\left\{-\sin e + \frac{\mu_2}{\mu_1} \cdot \frac{\mu_1'}{\mu_2} \cdot \sin e'\right\}} \quad . \quad . \quad . \quad . \quad (11)$$

where μ_1 and e are the index and emergent angle of the substance under test, while μ_1' and e' are the similar quantities for the standard substance employed in calibrating the block.

We find from equation 11 that in the case of a 90° block of $\mu_2 = 1 \cdot 75$ which has had its index determined from measurements on quartz, for which $\mu_1' = 1 \cdot 54$, that the error in θ required to give an ultimate error of 0·00001 in the measured indices is 44″ for $\mu_1 = 1 \cdot 5$; ∞ for $\mu_1 = 1 \cdot 54$; 23″ for $\mu_1 = 1 \cdot 60$; 11″ for $\mu_1 = 1 \cdot 65$; and 6″ for $\mu_1 = 1 \cdot 7$.

Note that when the block is calibrated in situ in this way the tolerance in angle is in the worst case nearly three times what it is in the worst case when μ_2 is obtained by measurements independent of the block. The value of μ_2 should always, therefore, be found in this way, rather than by independent measurements on the glass employed before it is cut, in order to minimise the effect of error in angle on the subsequent measurements. Moreover, when a block has been re-surfaced so that the angle has to be measured anew, the calibration of μ_2 should also be repeated so as to introduce the error in μ_2 corresponding to any error in the θ measurement in order to gain the compensation just discussed.*

In the foregoing treatment we have considered the accuracy in the value of θ, which is required to give an accuracy of one unit in the fifth decimal place in the indices measured on the instrument. It was recently suggested by various experts that the present requirements from the point of view of the optical designer are certainty to 1 unit in the fourth decimal place for the absolute indices, and certainty in the fifth place for the dispersion data.

This standard will clearly be attained with much more latitude in the accuracy of the measurement of θ. As far as the effect on the absolute index is concerned we can multiply the tolerances already obtained by 10. In the case of the 60° block, with its own indices determined on the instrument, we have just seen that the tolerance is in the neighbourhood of 3 seconds for 0·00001 error in μ_1. Thus 30 seconds error would be required to throw μ_1 out by 1 in the fourth place.

It is necessary, however, to see whether an error in θ of this magnitude would affect the dispersion measurements in the fifth place. Suppose we have a block of which the indices for the A' and G' lines—the extreme range of wave-length with which we need concern ourselves—are 1·731 and 1·787 respectively, and that we are measuring on it a crown glass of low indices say 1·496 and 1·510 for the same wave-lengths. These are characteristic values. The error in μ_1 due to 1 second error in θ is $1/T_\theta$ and equals $\sqrt{\mu_2^2-\mu_1^2}/2{\cdot}06$.

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* Another important compensation effected in a similar way by calibration in situ—*viz.*, that of constant personal errors of setting—is referred to in the Discussion.

Substituting the values for the two lines

$$(\delta\mu_1)_{A'}=0{\cdot}425\,; \quad (\delta\mu_1)_{G'}=0{\cdot}462.$$

$$\therefore\ \delta\{(\mu_1)_{G'}-(\mu_1)_{A'}\}=0{\cdot}037 \text{ unit in fifth place.}$$

Thus to produce an error of 1 unit in the fifth place in the dispersion from A' to G' would require an error in angle of $1/0{\cdot}037=27$ seconds.

In a similar way, if we are measuring a hard flint of indices, say 1·610 for A' and 1·643 for G', we find that the tolerance in angle from the point of view of the dispersion is 33 seconds.

In deducing the effect on the dispersions we have neglected the compensating effect of the corresponding errors in μ_2 which are produced if the block is calibrated on the instrument. The values of $\dfrac{\partial\mu_1}{\partial\mu_2}$ and $\dfrac{\partial\mu_2}{\partial\theta}$, from which the compensation arises, vary so very little over the range of indices involved in the dispersion that the compensating term is the same for both wave-lengths. Thus, while the actual error in index due to a given error in θ is profoundly modified by measuring μ_2 on the block itself, the effect on the dispersion is unaffected.

We may thus say that for a 60° block if the error in the angle of the block is less than, say, 25 seconds the errors from this cause will not exceed 0·0001 in absolute index or 0·00001 in dispersion. The same figure clearly applies also to the 90° block since T_θ is independent of θ.

But the 60° block is evidently pre-eminently suited for an instrument to fulfil these modified requirements, since if we allow such a large tolerance in θ, its measurement to the necessary accuracy can be done quite easily on the scale of the instrument itself, and the only constant left to be determined accurately is the index of the block. By cutting this to 60°, so that these measurements can be made without reference to a standard substance, the instrument can be verified in every essential particular by the user himself

§ 6. CONCLUSIONS.

An effort has been made in the foregoing paragraphs to show that with proper care in the design and subsequent use of the Pulfrich refractometer it will give results accurate to the fifth decimal place, not only in the dispersion, as specially discussed above, but also in the absolute index. It is not suggested that this latter achievement is easy. The mechanical perfection in manufacture which it assumes necessitates the very highest class of workmanship; but it is not an impossibly high standard, and in view of the important advantages which the method possesses over any absolute method, the production of a really good instrument of the Pulfrich type is of the utmost importance.

With regard to the possibility of a still higher accuracy, it is improbable that absolute indices will ever be obtained closer than 0·00001 by any method of this type on account of the difficulties of measuring prism angles, &c. It should be possible, however, to increase the accuracy of dispersion measurements by increasing the total size of the optical parts in order to permit the use of a telescope of larger aperture and power.

If these were increased to three or four times the present sizes the dispersion measurements might be obtained to two or three units in the sixth place if the micrometer were sufficiently good for the purpose.

The Author would like to express his indebtedness to Mr. T. Smith for his interest in the Paper and for many helpful suggestions; and to Dr. J. S. Anderson, whose practical experience of the instrument has been of the greatest service in corroborating or modifying the Author's own conclusions.

ABSTRACT.

The Paper deals with points to be observed in the use and design of Pulfrich refractometers. A theoretical investigation of the various errors to which measurements are liable is included.

DISCUSSION.

Mr. F. SIMEON expressed his interest in the investigation of the effect of film angle and the use of various liquids to minimise it. Had the author considered the effect of a slight rounding or chamfering of the edge of the specimen on the result? With regard to the most suitable graticule for the instrument, they had recently experimented with a form which consisted of a rectangular recess in the edge of an opaque screen. The setting was made by making the edge of the coloured band, where it crossed the recess, continuous with the edge of the screen. Except where it crossed the recess, the band was obscured by the screen. This gave very satisfactory settings. He agreed as to the improvement in the sodium setting when the bands were cut down to resolution point. He was interested in the discussion of micrometer errors. They (Messrs. Hilger) had had occasion to go into this carefully in designing their latest instrument. The condition they had adopted was that in which the *p* error was zero. The tangent error still remained; but as they had made θ_0 half the total range, the error at 5 deg. was only about half what it was in the author's curve. As regards the accuracy in the data for the blocks that makers might be able to supply in future, they had been able to obtain a melting of English glass which in no case showed variations of more than 0·000002 throughout. He had recently made absolute measurements on a prism of right-handed quartz for use as an auxiliary standard, and he was gratified to find that they agreed exactly with the values adopted at the N.P.L., as he had been somewhat uneasy about the discrepancies between his figures and those of other observers. The variation of his individual determinations had been about 0·000014. He observed that no reference to temperature occurred in the Paper. This was by no means a negligible factor in accurate work, especially in the case of quartz and the heavier flint glasses. Had the Author any suggestions as to the best means of temperature control? He suggested that some standard temperature, such as 20°C., should be adopted for the specification of refractive properties.

Mr. T. Smith said that no one reading the Paper could fail to conclude that a very extensive acquaintance with the instrument under all the conditions which could arise in practice, as well as a considerable amount of original investigation, lay behind it. The combination of the facilities for test work and research was essential to the proper consideration of a problem of this kind. This was only possible in an institution where work was carried on on an extensive scale. Unless his memory was wrong, the conclusions in this Paper were based on the experience gained in testing over 2,000 specimens of glass.

Mr. Lamplough (of Chance Bros., Ltd.) said he could confirm the advantage of using different liquids for the different kinds of glass. He had done this for the last six months or so, principally to avoid the shift in the bands produced by vibration and similar causes. He thought the 60 deg. prism would be more difficult to fit with a satisfactory water-jacket than the ordinary type.

Mr. L. C. Martin (communicated remarks) said that it seemed improbable that the types of setting employed in the Pulfrich instrument could ever be so satisfactory as the symmetrical settings possible in the ordinary spectrometer. There were uncertain amounts of irradiation at the retina and aberration in the system which must affect an unsymmetrical setting more adversely. Consistency was no doubt possible; but consistency required to be established between the refractometer and spectrometer indications before the former could be admitted as a standard instrument. We lost the difficulty of providing more than one good surface; but we had to accept certain constants of the instrument which could only be checked by further critical angle methods involving the same possibilities of error. The 60 deg. angle, while involving some loss of sensitiveness, would increase the range of the indications of the instrument, and would permit an interferometer examination of the prism in the required region, and also the determination of its constants on the spectrometer.

The Author, in reply, said that any chamfer on the edge of the specimen was fatal to accuracy, and it was their custom at the laboratory to reject any specimens that were not polished to an absolutely sharp edge. He was interested in Mr. Simeon's description of Hilger's new graticule. It would not, of course, minimise chromatic parallax effects, and seemed, as far as one could judge without experience, to be particularly prone to errors due to irradiation. Further, unless the length of the recess was very short, appreciable error might be introduced due to the curvature of the bands. To make the *p* error zero and $\theta_0=2\frac{1}{2}$ deg., as Messrs. Hilger had done, was undoubtedly the best method for a range of 5 deg., but he thought it was a great advantage to increase the micrometer range by an extra 2 deg. He was interested to find the close agreement of the values Mr. Simeon had obtained for quartz and those they had adopted at the laboratory. This certainly increased his confidence in these values. With regard to the question of temperature, the Paper was a somewhat long one, and in order to keep it within reasonable limits he had confined his attention to points that would, if attended to by the user or maker, produce some improvement in the accuracy of the results. This restriction excluded certain points equally vital to the complete treatment of the subject, but which, being inherent in the instrument, were beyond the control either of user or designer; and also those details, such as temperature conditions, which belong equally to all methods of refractometry, and are not, therefore, of special interest in connection with the Pulfrich refractometer. He was glad, however, that some of these points had been raised in the discussion. At present absolute indices were only specified to the fourth decimal place in routine determinations, and to this accuracy the effect of temperature was negligible within the ordinary range encountered in a laboratory. For accurate standardisation work it was necessary to take both temperature and pressure into consideration, since the indices μ_1 and μ_2 occurring in the equations are really the ratios of the indices of the substances to that of air. Thus we had to correct the values of the glass indices in accordance with the temperature coefficients of their indices relative to vacuum,* and apply a further correction for the variation in density of the air, which could be obtained by applying Gladstone and Dale's law. With regard to temperature control, he was convinced that the only accurate method with the Pulfrich instrument was to work at room temperatures. Not only was it impossible by any system of water-jacketing to produce a uniform temperature in a glass block of which one face must necessarily be exposed, but for accurate work it was also necessary to heat the air to the same temperature *right up to the object glass of the telescope.* He thought water-jackets should be dispensed with altogether, as they only tempted the unwary into thinking that temperature coefficients could be measured by their use. The first question raised by Mr. Martin is a point of great importance, though omitted from the Paper on the first of the grounds already explained. When conditions of definition and illumination are good—which they must always be for accurate work—an edge setting of the Pulfrich type can be *repeated* to practically the same accuracy as a symmetrical setting. With regard to irradiation, he had frequently tested the setting with the ordinary cross wires, and it does not vary to an extent that can be detected with bands varying in intensity within the range in which comfortable readings can be made. This being so, whatever personal error there is may be regarded as constant under ordinary good working conditions. As to its magnitude, an absolute test is clearly impossible until an instrument is made sufficiently good that the results are definitely free from all errors not inherent in the method; but there is evidence to show that the personal error is small. As far as our experience goes, settings made by different observers agree to within the limits of sensitivity; whereas when personal errors are large they usually vary considerably with different observers, as in the case, for example, of the unresolved sodium bands cited in the Paper. The author is of the opinion, from these and similar considerations, that the personal error of the setting does not amount to a tenth of a minute. It is interesting to point out, however, that whatever personal error exists is partially compensated in the same way as error in the angle of the block, provided the calibration of μ_2 is made on the instrument itself, because the error in e will be the same for the standardisation measurements as for the subsequent tests. From the curves and equations in the Paper it is easy to calculate that the constant error in e which will affect by 0·00001 the subsequent values of μ_1, when μ_2 is 1·75 is 100 seconds when $\mu_1 = 1·5$; 17 when $\mu_1 = 1·6$, 10 when $\mu_1 = 1·65$ and 6 when $\mu_1 = 1·7$. The compensation in the last case is negligible, but is appreciable for all the more usual glasses. As in the case of the θ compensation, calibration by means of an auxiliary substance is superior in this respect to the absolute method. Thus, for a 90 deg. block calibrated with quartz ($\mu_1 = 1·54$) the equivalent tolerance in personal error is 50 seconds for 1·5, ∞ for 1·54, 1,000 seconds for 1·6, 77 for 1·65 and 25 for 1·7. These figures are to slide rule accuracy only. This would be a really important advantage for the auxiliary substance method of calibration if there was any reason to believe that the personal error with this type of setting amounted to as much as a fifth of a minute.

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* These coefficients can be found for the different types of glass with sufficient accuracy in Hovestadts "Jena Glass."

XV. *On the Accuracy Attainable with Critical Angle Refractometers.* *By* FREDERICK SIMEON, *B.Sc.* (*From the Research Laboratory of Adam Hilger, Ltd.*)

RECEIVED FEBRUARY 6, 1918.

IT was suggested to the firm by Mr. Guild, of the National Physical Laboratory, that it would be advantageous to substitute a prism of 60° angle for the usual 90° prism used on a Pulfrich refractometer. The present investigation was undertaken in connection with this enquiry, but had been found desirable in dealing also with the Abbe refractometer and its modifications (Butter, Dipping, etc.) made by the firm, in which instruments, too, there is a possibility of using prisms of various angles.

The principle of the method of measuring the refractive index of any substance by observation of the critical angle with respect to it of a prism of higher, and known, refractive index is so convenient, and has found such wide application in instruments for technical and industrial uses, that it has seemed worth while to investigate the accuracy attainable by all instruments employing this method. All such instruments are provided with a prism having two polished faces, in contact with one of which the substance to be measured is placed. Light, which after passing through the substance enters the prism at grazing incidence, emerges from the second face of the prism, and it is this angle of emergence which is the quantity actually determined on the instrument. Various means are used to measure this angle, such as (i.) rotation of an observing telescope attached to a divided circle; (ii.) rotation of the prism by an arm passing over a scale of refractive index; (iii.) movement of the critical edge of the field over a scale in the eyepiece of the observing telescope, etc.; but these differences will be ignored in the present investigation, which concerns the prism system only.

The factors upon which the refractive index (μ) of the substance depends are :—

(*a*) The angle (θ) of the prism,

(*b*) The refractive index (μ_0) of the prism,

(*c*) The angle of emergence (i) of the critical ray from the second surface;

and it is sought to discover with what accuracy these quantities require to be known to ensure a given accuracy in μ; or, conversely, what accuracy in refractive index (μ) is attainable, assuming certain standard errors in these three data.

Consider now the passage of a critical ray through such a refractometer prism, and denote by r_1 and r_2 the angles which the ray inside the prism makes with the first and second surfaces respectively. By the law of refraction (*see* Fig. 1)

$$\mu \sin \frac{\pi}{2} = \mu_0 \sin r_1, \quad \ldots \ldots \tag{1}$$

$$\sin i = \mu_0 \sin r_2, \quad \ldots \ldots \tag{2}$$

and by geometry

$$r_1 + r_2 = \theta. \quad \ldots \ldots \ldots \tag{3}$$

Eliminating r_1 and r_2 between these three equations, we obtain

$$\mu = \sin \theta \sqrt{\mu_0^2 - \sin^2 i} - \cos \theta \, . \, \sin i. \quad \ldots \tag{4}$$

Differentiating (4) with respect to μ

$$\begin{aligned} 1 = {} & [\sqrt{\mu_0^2 - \sin^2 i} \, . \, \cos \theta + \sin i \sin \theta] \frac{\partial \theta}{\partial \mu} + \frac{\mu_0 \sin \theta}{\sqrt{\mu_0^2 - \sin^2 i}} \cdot \frac{\partial \mu_0}{\partial \mu} \\ & - \cos i \left[\frac{\sin \theta \sin i}{\sqrt{\mu_0^2 - \sin^2 i}} + \cos \theta \right] \frac{\partial i}{\partial \mu}, \quad \ldots \ldots \end{aligned} \tag{5}$$

or by slightly rearranging the terms

$$\begin{aligned} 1 = {} & \left[\frac{\sin \theta \, . \, \sin i}{\sqrt{\mu_0^2 - \sin^2 i}} + \cos \theta \right] \left[\sqrt{\mu_0^2 - \sin^2 i} . \frac{\partial \theta}{\partial \mu} - \cos i \frac{\partial i}{\partial \mu} \right] \\ & + \frac{\mu_0 \sin \theta}{\sqrt{\mu_0^2 - \sin^2 i}} \cdot \frac{\partial \mu_0}{\partial \mu} \quad \ldots \ldots \ldots \ldots \end{aligned} \tag{6}$$

It will be noticed that each term of (5) expresses the variation of μ with some one of the three fundamental data of the instrument.

In order to ascertain what accuracy can be relied on with any particular instrument, the value of i for least sensitiveness must be found, and this point will be investigated before the discussion of particular cases of the above expressions.

Assuming a particular prism (*i.e.*, θ and μ_0 constant for the time being), equation (5) reduces to

$$-\frac{\partial \mu}{\partial i} = \cos i \left[\frac{\sin \theta \sin i}{\sqrt{\mu_0^2 - \sin^2 i}} + \cos \theta \right]. \quad \ldots \ldots \tag{7}$$

Differentiating this with respect to i

$$-\frac{\partial^2\mu}{\partial i^2}=\sin\theta\left[\frac{\sin^2 i\cos^2 i}{(\mu_0^2-\sin^2 i)^{3/2}}+\frac{\cos^2 i}{\sqrt{\mu_0^2-\sin^2 i}}-\frac{\sin^2 i}{\sqrt{\mu_0^2-\sin^2 i}}\right]-\cos\theta\sin i \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

$=0$ when $-\frac{\partial\mu}{\partial i}$ is a maximum or minimum,

$$i.e., \cos\theta\sin i=\frac{\sin\theta}{\sqrt{\mu_0^2-\sin^2 i}}\left[\frac{\sin^2 i\cos^2 i}{\mu_0^2-\sin^2 i}+\cos^2 i-\sin^2 i\right]$$

$$\cot\theta\sin i\sqrt{\mu_0^2-\sin^2 i}$$

$$=\frac{\sin^2 i(1-\sin^2 i)+(1-2\sin^2 i)(\mu_0^2-\sin^2 i)}{\mu_0^2-\sin^2 i}$$

$$\cot^2\theta\sin^2 i(\mu_0^2-\sin^2 i)^3=(\sin^4 i-2\mu_0^2\sin^2 i+\mu_0^2)^2. \quad . \qquad (9)$$

This last equation is seen to be a quadratic in $\sin^2 i$, of which there are, in general, two real roots between 0 and +1. Upon substituting the corresponding four values of $\sin i$ into equation (8), it is found that two of these values are not solutions, while a third value does not correspond to a real direction of light in the prism. From a consideration of the change of sign of equation (7), it can be proved that the remaining value of $\sin i$ corresponds to a maximum value of $-\frac{\partial\mu}{\partial i}$—*i.e.*, it gives the value of i for least sensitiveness. It will be noticed that in the case of a 90° prism ($\cot\theta=0$) equation (9) takes a particularly simple form. One root only of the resulting quadratic in $\sin^2 i$ lies between 0 and 1, and only the positive value of the square root of this corresponds to a real direction of light in the prism, this value corresponding again to least sensitiveness. Thus, in cases of practical interest, there is as a rule a unique solution to the problem of determining the position of least sensitiveness.

As special cases of the above formulæ, 90° and 60° prisms of glasses of $\mu_0=1{\cdot}62$ and $\mu_0=1{\cdot}75$ will be considered. The various quantities occurring in equation (5) are given in the following table, in which are also included the various differential coefficients $\left(\frac{\partial\mu}{\partial\theta}\right)_{\mu_0 . i}$ denoting the partial differential coefficient of μ with respect to θ, both μ_0 and i being taken as constant, and so on.

μ_0.	1·62.		1·75.	
θ	90·0°	60·0°	90·0°	60·0°
i	48·5°	33·5°	48·0°	32·0°
$\sin\theta$	1·0	0·866	1·0	0·866
$\cos\theta$	0·000	0·500	0·000	0·500
$\cos i$	0·661	0·832	0·667	0·848
$\sin i$	0·748	0·552	0·742	0·529
$\sqrt{\mu_0^2-\sin^2 i}$	1·431	1·524	1·583	1·700
$\dfrac{\mu_0\sin\theta}{\sqrt{\mu_0^2-\sin^2 i}}$	1·131	0·922	1·106	0·892
$\dfrac{\sin\theta\sin i}{\sqrt{\mu_0^2-\sin^2 i}}+\cos\theta$	0·523	0·814	0·469	0·769
$\left(\dfrac{\partial\mu}{\partial\theta}\right)_{\mu_0,i}$	0·748	1·240	0·742	1·306
$\left(\dfrac{\partial\mu}{\partial\mu_0}\right)_{i,\theta}$	1·131	0·922	1·106	0·892
$\left(\dfrac{\partial\mu}{\partial i}\right)_{\theta,\mu_0}$	−0·346	−0·677	−0·313	−0·652

N.B.—The minus sign of the last quantity means, of course, that μ decreases as i increases, i being reckoned positive when on the side of the normal shown in Fig. 1.

Various deductions can be made from these figures. For example, the error in the measurement of refractive indices with a 90° prism owing to uncertainty in the value of the index of the prism itself is slightly greater than the amount of this uncertainty, and slightly less in the case of a 60° prism. Conversely, if the refractive index of the prism is to be determined

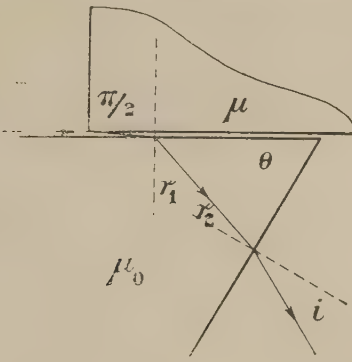

FIG. 1.

on the instrument itself by means of auxiliary standards, such as, for example, an accurately measured prism of quartz, then a more accurate value will be obtained in the case of a 90° prism than in that of a 60° prism.

Again, suppose that there is the same uncertainty in the measurement of i whatever the angle of the prism, then readings taken with a 90° prism will be twice as accurate as those taken with a 60° prism.

In order that errors from all these sources may be of the same importance, the angle of the prism must be known to twice the accuracy with which i can be measured. Supposing this last measurement to be made correct to 0·2 minute of arc (which represents about what can be done with the slow motion of the usual form of Pulfrich refractometer), then the angle of the prism should be known to $0{\cdot}1'=6$ seconds. The uncertainty in refractive index of the prism to give a similar error is about 0·00002 in the case of a 90° prism (0·2 minute = 0·00006 radian, approx.), while the corresponding value for a 60° prism is about 0·000045.

The curves in the accompanying diagrams give the variation with i of these differential coefficients for prisms of various refractive indices and angles. They are made to slide-rule

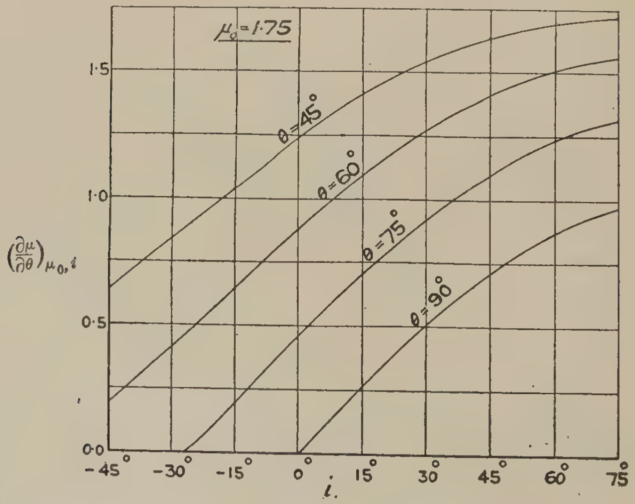

FIG. 2.

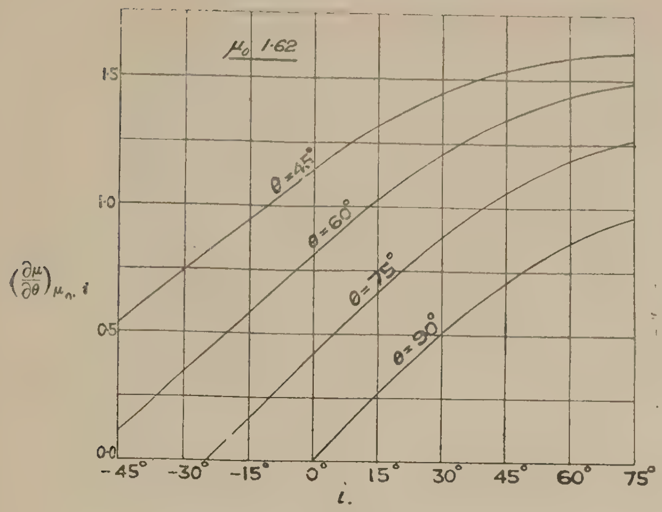

Fig. 3.

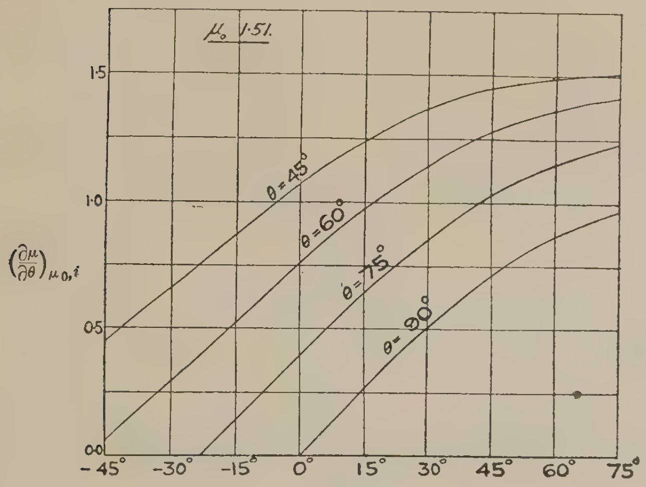

Fig. 4.

Figs. 2, 3 and 4 show the variation of measured refractive index with variation of refractometer prism angle for prisms of refractive indices 1·75, 1·62 and 1·51 respectively.

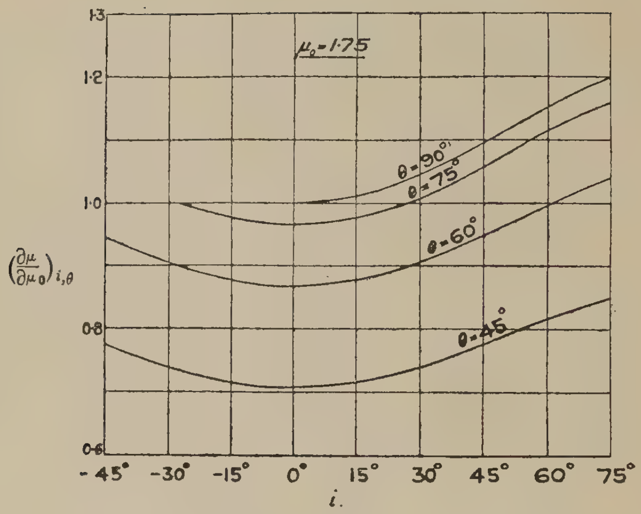
$\mu_0 = 1{\cdot}75$
1·3
1·2
1·0
0·8
0·6
$\left(\frac{\partial\mu}{\partial\mu_0}\right)_{i,\theta}$
θ = 90°
θ = 75°
θ = 60°
θ = 45°
-45°
-30°
-15°
0°
15°
30°
45°
60°
75°
i.

FIG. 5.

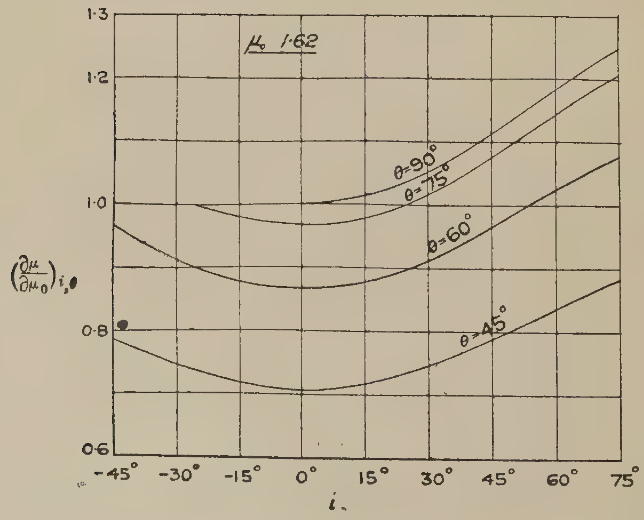
μ_0 1·62
1·3
1·2
1·0
0·8
0·6
$\left(\frac{\partial\mu}{\partial\mu_0}\right)_{i,\theta}$
θ = 90°
θ = 75°
θ = 60°
θ = 45°
-45°
-30°
-15°
0°
15°
30°
45°
60°
75°
i.

FIG. 6.

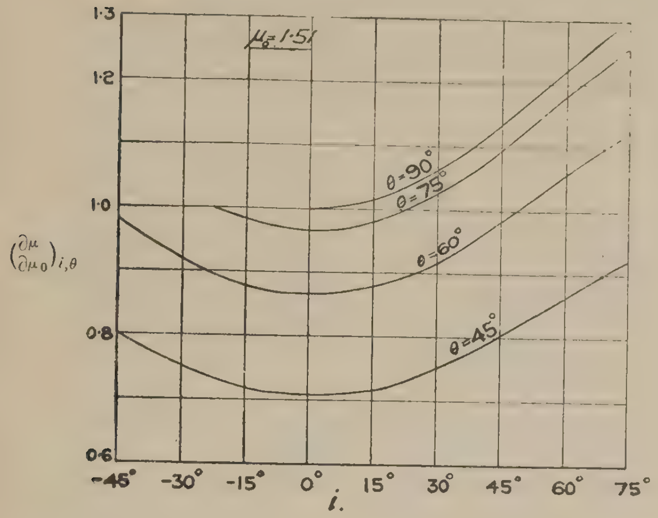

Fig. 7.

Figs. 5, 6 and 7 show the variation of measured refractive index with that of the refractometer prism for prisms of indices 1·75, 1·62 and 1·51 respectively.

accuracy only (as are the rest of the calculations), which is sufficient, as each is multiplied by a small factor in the estimation of errors. The most interesting ones are those connecting i and $\left(\frac{\partial\mu}{\partial i}\right)_{\theta,\mu_0}$.

The locus of the vertices of the curves for any given refractive index (μ_0) is obtained by eliminating θ between equations (7) and (9). The resulting expression is somewhat complicated, but it is seen that the locus is very nearly a straight line, the best straight line being shown dotted in the figures. It will also be seen that this line has very nearly the same slope whatever the value of μ_0. These loci are useful for interpolation of other prism angles.

The above considerations will indicate the nature of the factors controlling the design of prism systems for this class of instrument, having regard to the accuracy of measurement of i which is mechanically attainable.

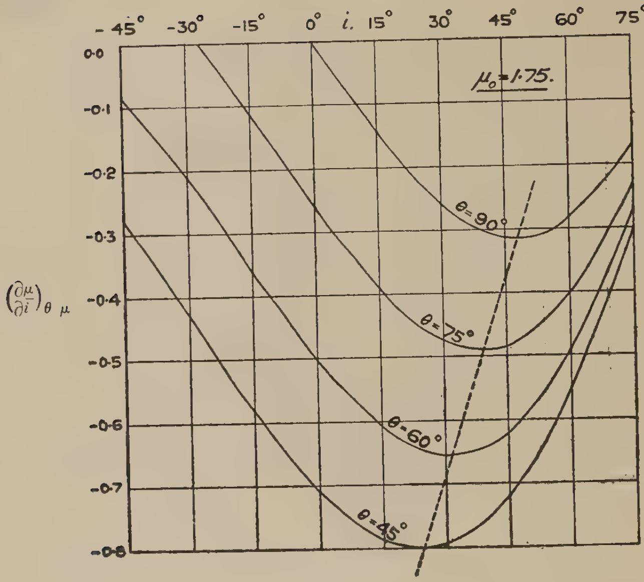
- 45°
-30°
-15°
0°
i.
15°
30°
45°
60°
75°
μ₀=1·75.
0·0
-0·1
-0·2
-0·3
-0·4
-0·5
-0·6
-0·7
-0·8
(∂μ/∂i)θ μ
θ=90°
θ=75°
θ=60°
θ=45°

FIG. 8.

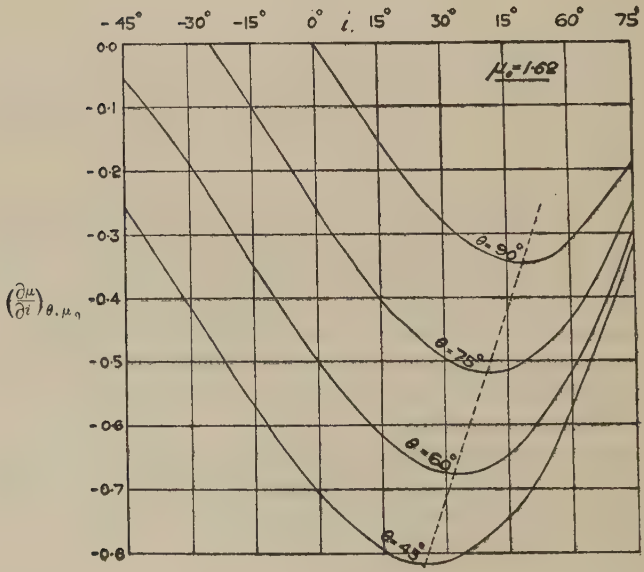
- 45°
-30°
-15°
0°
i.
15°
30°
15°
60°
75°
μ₀=1·68
0·0
-0·1
-0·2
-0·3
-0·4
-0·5
-0·6
-0·7
-0·8
(∂μ/∂i)θ.μ₀
θ=90°
θ=75°
θ=60°
θ=45°

FIG. 9.

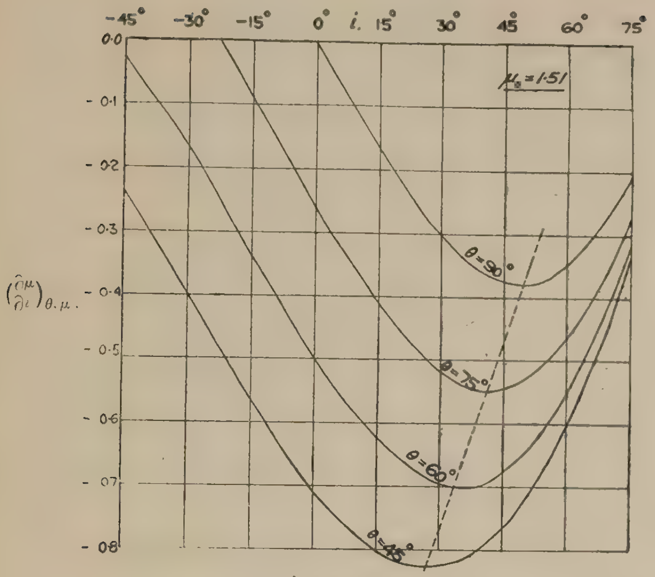

FIG. 10.

Figs. 8, 9 and 10 show the variation of measured refractive index with variation of angle of emergence of the critical ray from prisms of refractive indices 1·75, 1·62 and 1·51 respectively.

ABSTRACT.

The three factors controlling the determination of a refractive index by means of a critical angle refractometer are, so far as the prism system is concerned, (i.) the angle of the prism, (ii.) its refractive index, and (iii.) the angle of emergence of the critical ray from the second prism face. Expressions are obtained for the variation of the required refractive index with each of these factors separately and curves are given connecting these variations with the angle of emergence from the second prism face for various prism angles.

DISCUSSION.

Mr. T. SMITH thought it was unfortunate that the Author had plotted his curves against angles of emergence. What one wanted to know in practice were the values of these functions when determining a particular refractive index. The curves should, therefore, have been plotted against μ. As they appeared in the Paper they were misleading. The $\partial\mu/\partial\theta$ graphs, for instance, conveyed the impression that this quantity depended on θ, whereas in reality it depended only on μ_0 and μ, and had nothing to do with the angle of the prism. The mathematics could have been simplified somewhat. The investigation of the sensitiveness may conveniently start from the equation

$$\sin i=(\mu_0^2-\mu^2)^{\frac{1}{2}}\sin\theta-\mu\cos\theta, \qquad \text{. . . . .} \quad (1)$$

so that

$$-\cos i\frac{di}{d\mu}=\mu(\mu_0^2-\mu^2)^{-\frac{1}{2}}\sin\theta+\cos\theta \qquad \text{. . . . .} \quad (2)$$

showing that $\frac{di}{d\mu}$ is necessarily negative, since refraction in the way considered is only possible when θ is positive. Differentiating again to find the positions in which the sensitiveness is stationary,

$$\cos i\frac{d^2i}{d\mu^2}=\sin i\left(\frac{di}{d\mu}\right)-\mu_0{}^2(\mu_0{}^2-\mu^2)^{-\frac{3}{2}}\sin\theta, \quad . \quad . \quad . \quad . \quad (3)$$

showing that stationary values only occur with positive values of i. Differentiating a third time, and assuming $\frac{d^2i}{d\mu^2}=0$, leads to

$$\cos i\frac{d^3i}{d\mu^3}=\cos i\left(\frac{di}{d\mu}\right)^3-3\mu_0{}^2\mu(\mu_0{}^2-\mu^2)^{-\frac{5}{2}}\sin\theta$$

and therefore $\frac{d^3i}{d\mu^3}$ is necessarily negative when $\frac{d^2i}{d\mu^2}=0$. Since $\frac{di}{d\mu}$ is always negative, this shows that the stationary values are minimum values in absolute amount. The fact that $\frac{d^3i}{d\mu^3}$ has always the same sign is in itself sufficient to indicate that there is only one real solution to the equation $\frac{d^2i}{d\mu^2}=0$. The minimum sensitiveness can be expressed in terms of μ_0 and μ only by eliminating i and θ from equations (1), (2) and (3) when $\frac{d^2i}{d\mu^2}$ in (3) is equated to to zero. The elimination is, perhaps, most simply effected by combining (1) and (2) in the form

$$\sin^2 i+(\mu_0{}^2-\mu^2)\cos^2 i\left(\frac{di}{d\mu}\right)^2=\mu_0{}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Differentiating this with respect to μ, removing the common factor $2\cos i\frac{di}{d\mu}$, and putting $\frac{d^2i}{d\mu^2}=0$, gives

$$\left\{(\mu_0{}^2-\mu^2)\left(\frac{di}{d\mu}\right)^2-1\right\}\sin i=-\mu\frac{di}{d\mu}\cos i \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Introduce the factor $\sin^2 i+\cos^2 i$ on the right of (4), and eliminate i between (4) and (5). The result is obviously

$$(\mu_0{}^2-\mu^2)(x-1)^2(x-\mu_0{}^2)=\mu^2(\mu_0{}^2-1)x \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where x is written for $(\mu_0{}^2-\mu^2)\left(\frac{di}{d\mu}\right)^2$. The only roots of (6) which give a real solution to the problem are derived from positive values of x. The form of (6) shows that all positive values of x must exceed $\mu_0{}^2$. If $\mu_0{}^2+y$ were written for x, the terms in y^3 and y^2 would evidently have the same sign, and would differ in sign from the term without y. There is thus only one positive root of (6). The curve giving the corresponding value of $\frac{di}{d\mu}$ will pass through the lowest points of the curves A, B, C, D of Fig. 7 in Guild's Paper.* The value of θ with which these values of $\frac{di}{d\mu}$ are associated may be found from

$$\tan\theta=\frac{\mu(\mu_0{}^2-\mu^2)^{\frac{1}{2}}x}{(\mu_0{}^2-\mu^2)x-\mu_0{}^2}.$$

There is one further point of importance to which attention may be called. The minimum values of the sensitiveness given by the above formulæ are not absolute minima in the sense that higher values will be obtained by using a standard block of any other angle than that indicated. For in all cases

$$\frac{di}{d\theta}+(\mu_0{}^2-\mu^2)^{\frac{1}{2}}\frac{di}{d\mu}=0.$$

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* This Number, page 157.

Differentiating this with respect to μ leads to

$$\frac{d}{d\theta}\left(\frac{di}{d\mu}\right)=\mu(\mu_0{}^2-\mu^2)^{-\frac{1}{2}}\frac{di}{d\mu}$$

if $\frac{d^2i}{d\mu^2}=0$. Thus the sensitiveness determined by the condition $\frac{d^2i}{d\mu^2}=0$ is increased by increasing θ and decreased by reducing θ. Minimum sensitiveness in the absolute sense is given by the condition

$$(\mu_0{}^2-\mu^2)^{\frac{1}{2}}\frac{d}{d\theta}\left(\frac{di}{d\mu}\right)=\mu\frac{di}{d\mu}-(\mu_0{}^2-\mu^2)\frac{d^2i}{d\mu^2}=0,$$

which by the differential of (4) reduces to sin $i=0$, or $(\mu_0{}^2-\mu^2)\left(\frac{di}{d\mu}\right)^2=1$. Equation (4) shows that the latter solution is impossible. The minimum sensitiveness is given by

$$-\frac{di}{d\mu}=\mu_0(\mu_0{}^2-\mu^2)^{-\frac{1}{2}}$$

on a block whose angle θ satisfies $\mu_0 \sin\theta=\mu$ or $\sec\theta=-\frac{di}{d\mu}$. This result shows that Guild's curves A, B, C, D (Fig. 7) are touched by their envelope where the emergent ray is normal to the second face of the glass block. The same conclusions obviously follow from equation (4) without the need of differentiating with respect to θ.

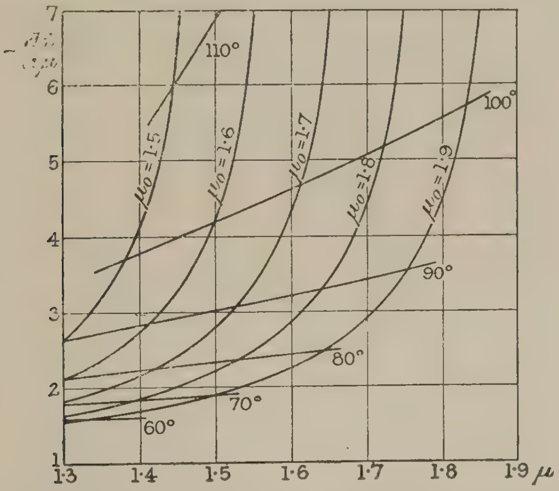

Diagram showing minimum values of the sensitiveness with two given kinds of glass, and the angles of the block to which they relate.

Example of use of diagram.—With a standard block of 80° angle and refractive index 1·9 the minimum sensitiveness is 2·5 (or 5 seconds for a fifth place unit in the index) and occurs for a specimen of approximate refractive index 1·64.

Mr. Lamplough said he had not used the new setting described by Mr. Simeon sufficiently to vouch for its accuracy, but it was certainly a very comfortable type of setting to use. He would like to know the purpose of serrating the edge of the shutter provided both in the Zeiss and Hilger instruments. What was the purpose in Messrs. Hilger's model of reversing the parts of the instrument right for

Mr. J. Guild thought that the Author, in finding the angle of emergence for minimum sensitivity, and comparing the liability to various errors, in these circumstances was comparing non-comparable quantities. It was true that the least sensitivity encountered in the working range of the instrument was an important factor in determining the relative advantages of different types; but the sensitivity minimum for the acute angled blocks occurred for values of μ quite outside the range for which blocks of that index would be used; in most cases they were even outside the range of indices found in solid or liquid substances. Thus the tabulated comparison of 60 and 90 deg. blocks was not valid, for the 60 deg. block ($\mu_0=1{\cdot}75$) was functioning under the condition $\mu=1{\cdot}18$, as against $\mu=1{\cdot}58$ in the case of the 90 deg. The corresponding figures for $\mu_0=1{\cdot}62$ were 1·04 and 1·43. Quite erroneous conclusions would be drawn from the tables. For example, one would gather that $\delta\mu/\delta\theta$ was much larger with 60 deg. blocks than with 90 deg. whereas this coefficient was independent of the angle, depending only on μ_0 and μ. The conclusions drawn by the Author were unduly in favour of the 90 deg. block for this reason. The curves as at present plotted required subsidiary calculation in order to obtain the information usually required.

Mr. J. W. French (of Messrs. Barr & Stroud); communicated remarks. The Author has confined himself to questions involved in the first design of the refractometer—that is, as regards the choice of the best prism angle. It would be very useful if he would extend the Paper to cover factors that determine the accuracy obtainable in the actual use of these instruments. These factors include: (1) The sharpness of the angle of the specimen; (2) the flatness of the contact surface of the specimen; (3) the flatness of the surface of the refractometer prism; (4) the accuracy with which the specimen is put into contact with the refractometer prism; (5) variations in the illumination; (6) errors in the quartz calibration prism; (7) temperature of the specimen; (8) temperature of the refractometer prism. Items (2) and (3) are of particular importance, considering the oblique transmission of the rays through a possibly curved surface. If these various items could be expressed in the same clear manner as those dealt with in the Paper it would be very helpful to users of such refractometers.

Mr. Churcher (of Bellingham & Stanley) said it had recently been observed by users of the Zeiss-Abbe refractometer that the instrument fails, owing to want of illumination, when measurements are required of liquids having an index exceeding 1·52. This was due to the substitution of a crown prism ($n_D=1{\cdot}52$) for the dense flint prism ($n_D=1{\cdot}75$), which was apparently used at first as the lower or illuminating prism. As is well known, in using the Abbe refractometer, one observes the border line of total reflection of a transparent substance in contact with a dense flint prism of known refractive index, light entering the substance at grazing incidence. In order to facilitate the entrance of light in the case of liquids, a lower prism of similar shape and size to the upper is placed in contact with it, the film of liquid being between the surfaces of the two prisms. The contact surface of the lower prism is left unpolished, and is intended to act as a scattering surface. If the scattering action were perfect, the refractive index of the lower prism would be immaterial. In the process of cleaning the ground glass surface, the sharp points are removed while the depressions remain. Such a surface approximates to a polished surface, especially at oblique illumination. Thus, if the index of the lower prism is less than that of the liquid film, the bulk of the rays entering the film are bent towards the normal at the interface, and cannot strike the second prism surface at grazing incidence. It is only when the lower prism is of higher index than the liquid that the light, being bent away from the normal, can enter the film in any quantity in a direction parallel to the interface so as to strike the second surface at grazing incidence. The Zeiss model was awkward to use with solid and plastic bodies such as glass, resins, gums, &c., as the prism box is designed to open towards the operator and away from the source of light. It is necessary in these cases to turn the instrument round, relying for illumination on the light reflected from the grey surface of the lower prism and to read the scale backwards. It is plainly stated in the Zeiss catalogue that the Abbe refractometer may be used for the measurement of the refractive indices of liquids from 1·30 to 1·7, and that the liquid to be examined is enclosed between two flint glass prisms. As neither of these statements is correct, it shows that manufacturers taking up the supply of instruments in the interests of British trade would do well to avoid the tendency to accept the optical and mechanical design of German instruments as incapable of improvement. It would be preferable to consult users of the instruments, and from accumulated experience to introduce entirely new designs, embodying as far as possible any suggestions which increase the utility and ease of manipulation of the apparatus.

The AUTHOR, in reply, said: Mr. Guild's remark concerning the subsidiary calculation necessary to determine the refractive index for which the sensitiveness is a minimum was quite justified. Nevertheless, the angle of emergence was a quantity which had been found useful in considering points in the design of refractometers. In reply to Mr. Lamplough's questions, the purpose of the serrated edge to the shutter was to enable distinction to be made in the two edges of a coloured band in the field of view, the unimportant edge only being affected by interposition of the shutter. It was not, of course, necessary for a practised observer. The purpose of reversing the parts of the instrument in Messrs. Hilger's new model was to bring all screw heads, &c., within reach of the observer's right hand. Additional support had been given to the various attachments, and a greater useful range of movement of the telescope provided. With regard to Mr. French's remarks, the Paper only attempts to deal with points in the first design of such instruments. The other factors named are of great importance in practice, and mention of several of them has been made in connection with the preceding Paper, though a fuller discussion is undoubtedly desirable.

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